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A Highly Sensitive Detection Method for Temperature Programmed Oxidation of Coke Deposits: Methanation of CO_2 in the Presence of O_2

S. C. FUNG AND C. A. QUERINI

Exxon Research and Engineering Company, Corporate Research Laboratories, Route 22 East, Annandale, New Jersey 08801

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Temperature programmed oxidation is the most widely used technique in the study of coked catalysts. This technique provides useful information about coke distribution and coke type on the catalyst surfaces. A new detection method, which gives continuous monitoring of coke oxidation rate, has been applied to this technique. The new detection method is simple and highly sensitive. It consists of a methanator and a flame ionization detector. It involves the conversion of CO_2, an FID insensitive gas, to an FID sensitive gas, CH_4, in the presence of an oxygen-containing carrier gas. It has been found that the conversion efficiency of the methanator strongly depends on oxygen concentration, its flow rate, and the temperature of the methanator. At temperature below 673 K and at <3% O_2, the incomplete conversion of CO_2 to CH_4 is mainly due to kinetic limitations brought about by the excess water produced in the methanator from the oxygen in the carrier gas. At higher temperatures and O_2 concentrations, equilibrium limits the conversion of CO_2 to a low level. Complete conversion of CO_2 to CH_4 is realized when O_2 < 3%, carrier gas at 20–60 cc/min, and methanator at 673 K.

INTRODUCTION

In any hydrocarbon processing, coke deposition leading to catalyst deactivation is seemingly unavoidable. Therefore, a considerable effort has been focused on the characterization of carbonaceous deposits. Different techniques were used to obtain information about the location, composition, and structure of coke deposits, e.g., TEM (*1–3*), Laser Raman Spectroscopy (*4*), EELS (*5*), and ^{13}C NMR (*6*). However, the most widely used technique is temperature programmed oxidation (TPO). This technique has been used to study coke on naphtha reforming catalysts (*7–11*), zeolites (*12*), Ni catalysts (*13, 14*), etc. Currently, TPO is performed with the following detection methods:

—determination of CO_2 by a thermal conductivity detector (TCD) after it is separated from oxygen in a GC column (*8*);

—quantification of CO_2 with a mass spectrometer (*15*);

—monitoring temperature increment above a reference sample, in differential thermal analysis (DTA) equipment (*9*);

—measurement of weight loss in thermal gravimetric analysis (TGA) equipment (*16*).

The detection of CO_2 using a TCD requires the separation of CO_2 from O_2 via a GC column and, therefore, is a noncontinuous analysis. This analysis misses the fine structure, peak height, and peak temperature. The use of a mass spectrometer makes it possible to sample in intervals of a few seconds, but it is not as simple as TCD. During differential thermal analysis, metal, sulphur, and contaminants contribute to the signal. Additionally, it is very difficult to determine kinetic parameters. In thermal gravimetric analysis, plug flow through the sample is often not possible and thus the coke oxidation kinetics are greatly influenced by oxygen diffusion. Also this tech-

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nique has limited sensitivity and the weight loss does not always result from burning off coke deposits: interference from metal oxides formation, dehydroxylation of the support, and sulfur oxidation.

In this paper we describe a new detection method which is simple and highly sensitive for TPO of coke deposits. The unit consists of a Model AMI-1 temperature programmed apparatus, manufactured by Altamira Instruments, Inc., and a computer-controlled valving system for the selection of the desired gas stream among many to the sample cell. Without modifications, the AMI-1 apparatus is not suitable for analysis of coke deposits since it has only a TCD and is without a GC column. The new detection scheme involves the conversion of CO_2, a flame ionization detector (FID) insensitive gas, to an FID sensitive gas, CH_4, in the presence of an oxygen-containing carrier gas. This is achieved by the addition of a small reactor, filled with a Ru catalyst, and placed after the sample cell. When hydrogen is added to the reactor, the Ru catalyst hydrogenates CO_2 to CH_4 quantitatively. The CH_4 generation rate is continuously monitored by an FID. A GC column is not needed, because FID is not sensitive to O_2 and H_2O present in the gas stream coming from the sample cell.

Group VIII metals have been used for the hydrogenation of CO_2 to CH_4 (*17–20*). Ruthenium and rhodium were found to have the highest activities and selectivities for this reaction (*21*). *All the above studies were performed without a continuous flow of oxygen to the methanation catalysts.* In TPO of coke deposits, the gas coming from the sample cell contains oxygen, since excess oxygen is required in the TPO experiments. Therefore, it is necessary to study the influence of oxygen in the hydrogenation of CO_2 to CH_4 and to establish the optimum condition for TPO experiments in connection with the new detection method. The improvements in sensitivity and spectrum resolution obtained by the new detection method are demonstrated when they are compared with spectra obtained by a TCD (via a GC column), TGA, and DTA.

EXPERIMENTAL

TPO of Catalyst Coke Deposits

Figure 1 shows a diagram of the modified TPO unit. This unit is controlled by a computer. A multivalving system allows the selection of the desired gases to be used in the experiment. The coked sample, about 20 mg, is loaded in a U-shaped quartz cell, which is placed in a furnace. One to two grams of coked catalyst in the form of $\frac{1}{16}''$ extrudates were ground, thoroughly mixed, and reground and remixed to yield a fine powder which passed through an 80-mesh screen. The fine powder was compressed to a pellet in a 1" die at a pressure of 20,000 psi. The pellet was broken up to small particles which were passed through a 60-mesh screen and retained by an 80-mesh screen. During the preparation of the sample, care has to be taken not to introduce carbon-containing material, such as oil from the fingers, into the sample. The preparation and loading of the sample into the sample cell are done with contact only to clean glass, ceramics, and metal surfaces free of carbon contaminants. There is no need for catalyst pretreatment before TPO. This sampling method gives highly reproducible results.

In a standard TPO, a helium carrier gas containing a low concentration of O_2 is fed into the cell at a constant flow rate (in the range of 20–80 cc/min). It has been determined that at a carrier gas flow rate of 60 cc/min, it takes about 12–15 sec for the gas to go from the sample cell to the FID. Therefore, the time delay in the FID signal shifts the TPO spectrum to a higher temperature by 2–3 K when the temperature ramp rate is 13 K/min. The sample temperature is increased linearly at the desired heating rate from room temperature to a high enough final temperature at which complete oxidation of all the carbon deposits occurs. The exit gas consists of a mixture of CO_2, O_2, H_2O, and He. This mixture then proceeds to

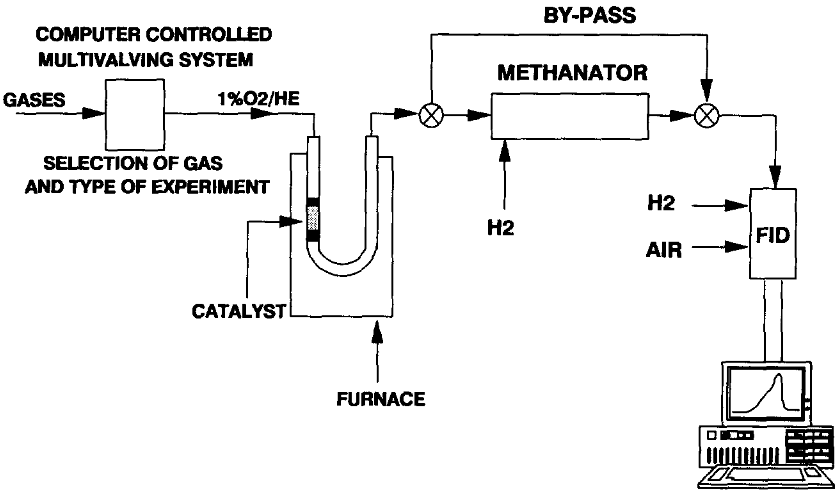

FIG. 1. Diagram of temperature programmed oxidation unit.

a reactor, called a methanator, that contains about 0.5 g of 40-wt% Ru/zeolite-13X. A pure H_2 stream at 22 cc/min is also injected into the methanator, where CO_2 is transformed into CH_4 and oxygen in the carrier gas to water. The combined stream flows directly into an FID. This stream supplies the FID with the major portion of hydrogen required for stable flame operation. Supplementary hydrogen, at a low flow rate, can be added to the FID through a separate flow control. In certain experiments when the gas exited from the sample cell bypasses the methanator and goes directly to the FID, the supplementary hydrogen becomes the sole source of hydrogen for the FID and should be adjusted to a higher flow rate.

The methane generation rate, i.e., coke oxidation rate, is continuously monitored by an FID, Model 12-800, manufactured by Gow-Mac Instrument Co. The FID signal is controlled by an electrometer (Gow-Mac), Model 40-900. A computer is used to store and display the FID signal as a function of sample temperature.

To compare with this new detection method, TPO experiments of the same coked catalysts were carried out using other detection methods. In one of the methods, the level of CO_2 in the gas exiting from the sample cell was periodically measured by a TCD after it was separated from oxygen and water by a $10' \times \frac{1}{8}''$ stainless steel GC column packed with 100/120 mesh HayeSep D. Experiments involved the indirect methods of monitoring the oxidation of coke were performed using differential thermal analyses and thermal gravimetric analyses in a Mettler TA2000C. About 100 mg of a coked catalyst was used in these experiments.

Methanation Activity

(*A*) *Determined by pulse CO_2 reaction.* The activity of the above Ru catalyst in the methanator was studied by means of pulse reaction employing 100-μl pulses of varying CO_2 concentrations injected into a helium carrier gas stream which flowed directly into the methanator, i.e., the carrier gas did not go through the sample cell (this flow path is not shown in Fig. 1). The effects of the oxygen concentration in the helium carrier gas, its flow rate, and the methanator temperature on the hydrogenation efficiency of the Ru catalysts were studied. Quantification of the measurements was possible through calibrations obtained by the injection of pulses of a known quantity of CH_4 to the FID (bypassing the methanator) using the same carrier gas and carrier gas flow rate.

(*B*) *Determined by temperature programmed methanation.* Temperature programmed methanation (TPM) experiments were used to define the optimum methanator temperature for the conversion of CO_2 to CH_4 and the stability of the ruthenium catalyst. A sample of the Ru catalyst of 0.1 g was placed in a quartz cell. After hydrogen reduction, a gas mixture of 70% H_2, 10% CO, 10% CO_2, and 10% He was fed to the catalyst and the temperature was increased from room temperature to 873 K at 10 K/min. The gas exited from the sample cell went directly to the FID (bypassing the methanator) since the Ru catalyst in the sample cell acted as the methanator. The effect of various pretreatments on the Ru hydrogenation activity was also studied.

RESULTS AND DISCUSSION

Massive Ru/Zeolite-13X Methanation Activity

(*A*) *Influence of oxygen concentration.* The influence of the oxygen concentration on the hydrogenation activity of the Ru catalyst was studied using pulses of CO_2 in an oxygen-containing carrier gas. Pulses of 1%, 2%, and 4.26% CO_2 (in helium) were sent to the methanator by a pure helium carrier gas (no oxygen) or by a helium carrier gas containing 0.5%, 1%, or 3% O_2. Later in this section, it is shown that the complete conversion of CO_2 to methane requires that the concentration of oxygen in the carrier gas to be below 3%. Under this condition, the maximum CO_2 concentration produced at any instant in a TPO experiment is 3%, even when all the oxygen is consumed by the coke deposits. Usually, the TPO experiment is carrier out with an appropriate amount of catalyst and a high enough carrier gas flow rate so that at any instant the maximum amount of oxygen consumption is less than 20% to avoid mass- and heat-transfer limitations. Therefore, conversion study using CO_2 concentration higher than 4.26% in the pulse is not necessary.

The CO_2 pulse was introduced to the methanator by a carrier gas flowing at 60 cc/min. Hydrogen was supplied to the methanator at 22 cc/min. The methanator was at 673 K. Results are shown in Table 1. The CO_2 pulses (1 to 4.26% CO_2) were completely converted to CH_4 when pure helium was used as the carrier gas. Complete conversion of CO_2 was also obtained with the 0.5 and 1% O_2/He carrier gas. However, when the oxygen concentration is increased to 3%, not all the CO_2 is hydrogenated. The conversion levels for the 1, 2, and 4.26% CO_2 pulses were 63, 61, and 55%, respectively.

Table 1

Effect of O_2 Concentration in the Hydrogenating activity of Ru/Zeolite-13X

Pulses	% CO_2 Transformed			
	Helium	0.5% O_2	1% O_2	3% O_2
1% CO_2	100	100	100	63
2% CO_2	100	100	100	61
4.26% CO_2	100	100	100	55

Note. Temperature, 673°K; carrier flow rate, 60 cc/min.

Possible reasons for this behavior are: (a) thermodynamics: displacement of the equilibrium of the hydrogenation reaction because of the presence of water; (b) formation of an inactive oxide layer on the ruthenium surface; (c) reduction of CO_2 hydrogenation rate due to oxygen or its oxidation product, water.

In case (a), water produced in the methanator because of oxygen in the carrier gas may decrease the equilibrium conversion of CO_2 to CH_4 according to reaction (1):

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O. \qquad (1)$$

The higher the O_2 concentration, the higher the amount of water and as a consequence, the effect on the equilibrium is more pronounced. To see how important this effect is, equilibrium conversions for reaction (1) were calculated for various temperatures, oxygen, and CO_2 concentrations. The con-

TABLE 2

Calculated CO_2 Equilibrium Conversion in the Methanation Reaction (1)

O_2 Conc. (%)	CO_2 conversion (%)					
	1% CO_2			4% CO_2		
	593 K	673 K	703 K	593 K	673 K	703 K
0	100	99.99	99.98	99.99	99.60	98.52
1	100	99.98	99.91	99.99	99.13	96.91
3	99.99	99.85	99.40	99.94	96.26	90.06
10	99.74	86.00	66.45	78.00	49.70	37.32
Eq. Constant	1.12×10^5	1.45×10^3	3.61×10^2			

version of oxygen to water was assumed to be complete and according to reaction (2):

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O. \qquad (2)$$

Hydrogen concentration in reaction (1) was chosen to be the same as that experienced in the methanator, i.e., 27%. Though the equilibrium calculation is based on a homogeneous gas mixture which pulse reaction could not attain, it represents the upper limits of O_2 concentration in the pulse. The results are shown in Table 2. It can be seen that the equilibrium conversion of the CO_2 to CH_4 depends on the concentration of O_2, CO_2 and the reaction temperature. Within a temperature range from 593 to 673 K and O_2 concentration from 0 to 3%, the lowest equilibrium conversion of CO_2 is 96.26% when the initial CO_2 concentrations is 4%. Under similar conditions, the CO_2 pulse hydrogenation experiments gave significantly lower CO_2 conversion, i.e., from 55 to 63% when O_2 was at 3% (Table 1). Therefore, equilibrium limitation is not the cause of incomplete conversion of the CO_2 pulses when O_2 concentration in the carrier gas is $\leq$ 3%. However, equilibrium limitation is significant at moderate CO_2 and O_2 concentrations when the methanator temperature is at or above 703 K. In particular, when O_2 is increased to 10%, equilibrium limitation becomes important and limits CO_2 conversion values to 86–37%. Based on equilibrium calculations, the TPO experiments should be carried out with $\leq$3% O_2 in the carrier gas and methanator temperature below 703 K.

In case (b), the possibility of formation of an inactive oxide layer on the surface of the ruthenium when oxygen is in the carrier gas was explored by doing oxidation–reaction cycles. In one experiment, 100 mg of the Ru catalyst was oxidized in the sample cell using 1% O_2, heating from room temperature to 673 K at 10 K/min, and holding at the final temperature for 30 min. After this treatment, the catalyst was cooled in helium and a temperature programmed methanation (TPM) was done. The catalyst was heated from room temperature to 873 K at 10 K/min. A mixture containing 70% H_2, 10% CO, 10% CO_2, and 10% He was passed over the catalyst at 20 cc/min. Within the limited range of space velocity in our equipment, high CO and CO_2 concentrations give a better discrimination of catalyst activity with increasing temperature. Otherwise, at low CO and CO_2 concentrations, complete conversion may occur at low temperatures and, therefore, increases in activity at higher temperatures cannot be observed. The amount of methane produced was monitored continuously with an FID. The same experiment was done with another sample of the same Ru catalyst which was oxidized with 1% O_2 to a final temperature of 873 K. Figure 2 shows the results of these two experiments. Both samples show similar be-

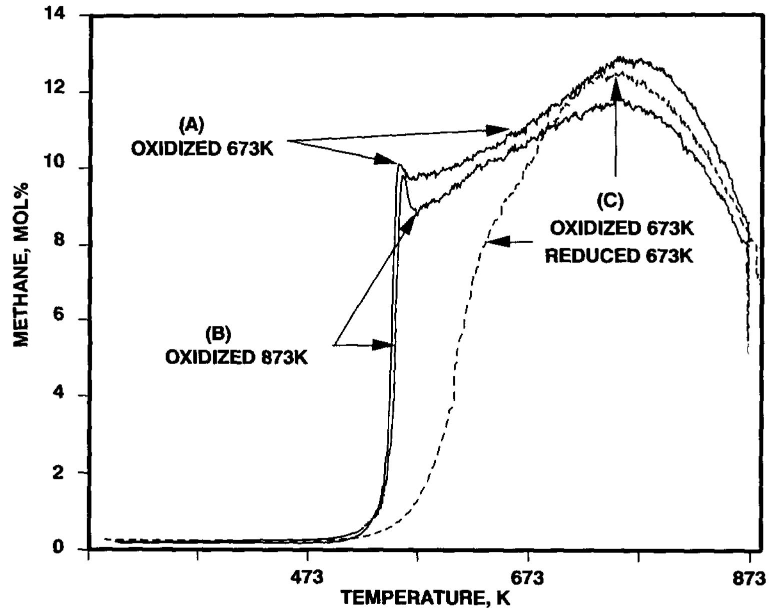

FIG. 2. Methane production in temperature program methanation experiments. Feed, 70% H_2 + 10% CO + 10% CO_2 + 10% He; flow rate, 20 cc/min; heating rate, 10 K/min. Pretreatments: samples preoxidized with 1% O_2/He heating at 10°K/min from room temperature to 673 K (A) and 873 K (B), holding at the final temperature for 30 min. Sample (C) preoxidized the same as (A) followed by a reduction with pure hydrogen, heating at 10 K/min from room temperature up to 673 K, and held for 10 min.

havior. Below 523 K, there is no activity for the methanation reaction. Above this temperature, there is a sudden increase in the activity followed with a slow increase to a maximum at 753 K. Exothermicity in the reduction process of RuO_2 may cause the sudden increase in methanation activity. However the small sample size should minimize this effect. The drop in the methanation activity at temperature higher than 753 K is due to thermodynamics limitations (*22*). When these two TPM spectra are compared with the TPM spectrum of a sample preoxidized and then reduced at 673 K, one notes that the oxidized samples have higher methanation activities than the reduced sample (Fig. 2). Based on this observation, the incomplete conversion of CO_2 pulses to CH_4 at 3% O_2 is not due to inactive oxide layer formed on the Ru catalyst.

The increase in the methanation rate with temperature is much slower for the reduced sample than the oxidized samples. The increase in the methanation rate with temperature of the reduced catalyst may be due to more metal sites being available for hydrogen adsorption since CO coverage is lower at higher temperature. Thus, the steep jump in the methanation activity of the oxidized samples may be the result of availability of activated hydrogen during the reduction process of RuO_2. The reduction process, which increases the availability of adsorbed hydrogen, proceeds within an appreciable temperature range, and that is why the methanation activity of the oxidized samples is higher than the reduced sample from 523 to 673 K. Another possible explanation is that the reduction of RuO_2 in the presence of CO and CO_2 during the TPM experiment produces Ru crystallites with topology different from the one obtained under pure hydrogen (*23*). This "preferred crystal orientation" gives much higher methanation

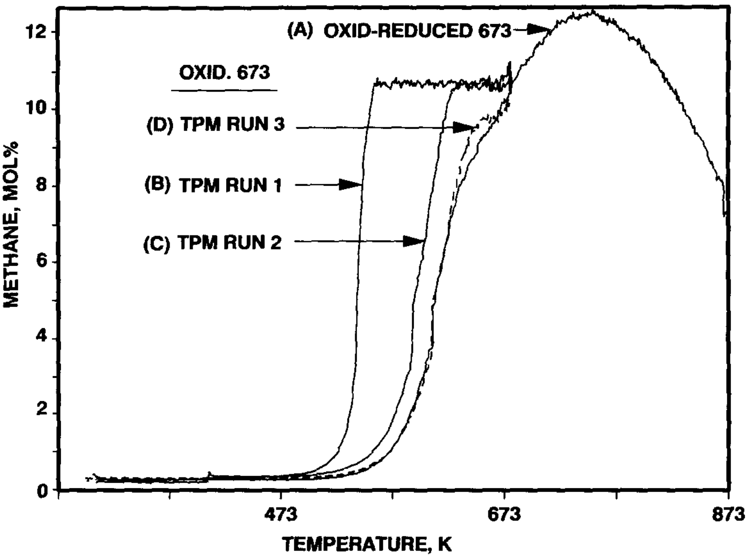

FIG. 3. Methane production in TPM experiments, same conditions as in Fig. 2. (A) Same experiment as (C) in Fig. 2; (B) sample preoxidized up to 673 K, holding at final temperature for 5 min, followed by TPM; (C) second TPM of (B); (D) third TPM of sample (B).

activity. It should be able to maintain this preferred crystal orientation after the 1st TPM when the first TPM is carried out to 673 K which is well below the temperature at which sintering of Ru crystallites occur. A second TPM, after the catalyst was cooled under the above mixture, should give the same spectrum as the first TPM. Figure 3 shows that the second and third TPM when ramped up to the same final temperature as the first, shifted to substantially higher temperatures from the first TPM. The third TPM matches exactly with the profile obtained previously with the preoxidized and then hydrogen reduced sample. This suggests that complete reduction of RuO_2 in the preoxidized sample, under TPM condition, is realized only after the second TPM. Thus, the steep jump in the methanation activity of the oxidized sample is mainly due to increase in the availability of activated hydrogen during the reduction process of RuO_2.

In case (c), CH_4 or CO, the latter being an intermediate compound in CO_2 hydrogenation (*17, 19*), may compete successfully with hydrogen for oxygen at high O_2 concentrations and therefore, 100% conversion of CO_2 is not possible. The reactions that need to be considered are:

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (3)$$

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \quad (4)$$

$$H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O \quad (2)$$

$$CO + \tfrac{1}{2}\,O_2 \rightarrow CO_2 \quad (5)$$

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \quad (6)$$

The equilibrium constants for reactions (2), (5), and (6) are very high and practically these three reactions can be considered irreversible. Therefore, it is expected that when the residence time is increased, oxygen should be totally converted in the inlet section of the methanator, and downstream from the inlet only reaction (3) and (4) can proceed. To verify this hypothesis, experiments at a lower carrier gas flow rate were attempted. Table 3 shows when 3% O_2 is in the helium carrier gas, complete conversion of the 4.26% CO_2 pulse at 673 K is possible only if the carrier gas flow rate is lowered

TABLE 3

Effect of Carrier Gas Flow Rate on CO_2 Conversion of 4.26% CO_2 Pulses

Carrier (% O_2)	Temp. (K)	CO_2 Conversion (%) Carrier flow rate	
		60 cc/min	20 cc/min
1	623	82	100
3	673	55	100

from 60 to 20 cc/min. The same effect is observed with 1% O_2 in the helium carrier gas at 623 K. This indicates that the incomplete conversion of the CO_2 pulse is definitely due to kinetic limitations. Thus, for a complete conversion of CO_2 to CH_4 when using higher O_2 concentration, it is necessary to decrease the flow rate of the carrier gas. Other possibility, as shown later, is to increase the methanator temperature.

One possible pathway for incomplete CO_2 conversion is due to the effect of water on the methanation rate of the ruthenium catalyst according to reactions (3) and (4). Reaction (3) is fast compared to reaction (4). Under steady-state conditions, CO attains an equilibrium concentration according to reaction (3) which has an equilibrium constant of 0.08 at 673 K (*24*). The presence of water, formed by the reaction of O_2 in the carrier gas with hydrogen in the methanator, lowers the steady-state concentration of CO and thereby decreases the methanation rate. This was demonstrated with 4.26% CO_2 pulses using helium carrier gas saturated with water at room temperature (2.6% water in helium). Results are included in Table 4. Only 75% CO_2 conversion was obtained at 623 K with water-saturated helium. This is in good agreement with the 82% CO_2 conversion obtained using 1% O_2/He, which yields a lower water concentration of 2%. Therefore, water inhibition of the methanation rate of ruthenium catalyst is the major reason for incomplete conversion of CO_2 to CH_4 in an oxygen containing carrier gas. This restricts oxygen concentration to below 3% when Ru/zeolite-13X is used as the methanation catalyst. If higher oxygen concentration is desired, it is still possible to obtain complete CO_2 methanization if an oxygen trap is installed in front of the methanator. Such a trap quantitatively removes oxygen without altering the CO_2 concentration in the gas exiting the sample cell. Metals and metal oxides should be the right candidates, e.g., massive nickel catalysts.

(*B*) *Influence of temperature.* In Table 4, results of the hydrogenation of pulses of 4.26% CO_2 in the methanator at 623 and 673 K are shown. Using helium as carrier gas, total conversion of CO_2 to CH_4 occurs at both temperatures. When using 1% O_2/He as carrier gas at 60 cc/min, complete CO_2 conversion is maintained at 673 K but not at 623 K. The lower temperature case gives a CO_2 conversion of 82%. As shown in Table 3, CO_2 conversion at the lower temperature can be improved to 100% when the 1% O_2/He flow is decreased to 20 cc/min. The favorable effect of increasing temperature and decreasing flow rate on CO_2 conversion indicates that the limitation in CO_2 conversion in the presence of O_2 is a kinetic phenomenon.

A temperature programmed methanation experiment was carried out up to 873 K to define the optimum temperature for methanation using a hydrogen-reduced Ru catalyst. Figure 4 shows the results of three consecutive TPM experiments on the same sample, with no pretreatment in between runs. In the first run a maximum is obtained

TABLE 4

Effect of Temperature and H_2O on CO_2 Conversion of 4.26% CO_2 Pulses

Carrier	Flow rate (cc/min)	Temp. (K)	Conversion (%)
1% O_2/He	60	623	82
1% O_2/He	60	673	100
He	60	623	100
He	60	673	100
He + 2.6% H_2O	60	623	75
He + 2.6% H_2O	60	673	100

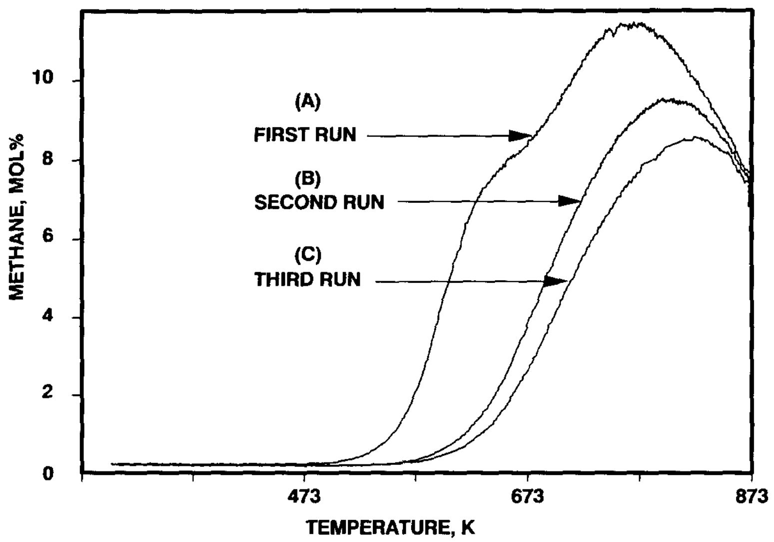

FIG. 4. Methane production in TPM experiments, same conditions as in Fig. 2. (A) Sample reduced at 673 K for 30 min; (B) second TPM of (A); (C) third TPM of (A).

at about 750 K. The second and third run show that the catalyst deactivates after heating up to 873 K. No coke was detected on the deactivated catalyst. Therefore, the deactivation is probably due to sintering of the Ru metal particles. Because of thermodynamics limitations, all three curves merge together at high temperature (*22*).

These results indicate that increasing the temperature up to 753 K, the activity of the catalyst increases, but the temperature has to be chosen as low as possible to avoid sintering of the Ru particles. It has been found that at 673 K the Ru/zeolite-13X catalyst provides sufficient rate to completely convert 4.26% CO_2 pulses to methane when oxygen in the carrier gas is below 3%. Under this condition, the methanation catalyst gives stable operation for more than 6 months if the catalysts being studied contain no sulfur or an effective sulfur oxide trap is installed in front of the methanator. The effectiveness of the methanation catalyst is determined twice a week by CO_2 pulse calibration. If the FID signal (area under the curve) is lower than the standard value by more than 10%, the catalyst in the methanator is changed to a new charge. Fresh Ru/zeolite-13X catalyst obtained from Gow-Mac gives consistent performance, i.e., complete conversion of CO_2 to methane under the above specified condition.

(*C*) *Influence of carrier gas flow rate.* Because the total flow that goes through the sample cell goes into the FID, the influence of the flow rate on the detector sensitivity has to be analyzed.

Experiments using pulses of 4.26% CO_2 and 1% CH_4 in a helium carrier gas at several flow rates were performed. Figure 5A shows the FID response to the same 100-μl 4.26% CO_2 pulse at various helium flow rates. It is obvious that enhanced response is obtained at high carrier gas flow rates. This is not due to inefficiency of the methanator since it should give the opposite effect, i.e., more complete conversion of CO_2 at lower space velocity. Additionally, using 1% CH_4 pulses directly injected into the FID (bypassing the methanator) gives similar effect. Figure 5B is a plot of the FID response to the CO_2 and CH_4 pulses, in terms of area/micromole of CO_2 or CH_4, at various carrier gas flow rates. Both gases give similar responses. Thus, the conversion of CO_2 is total at all flow rates. These results indicate that the

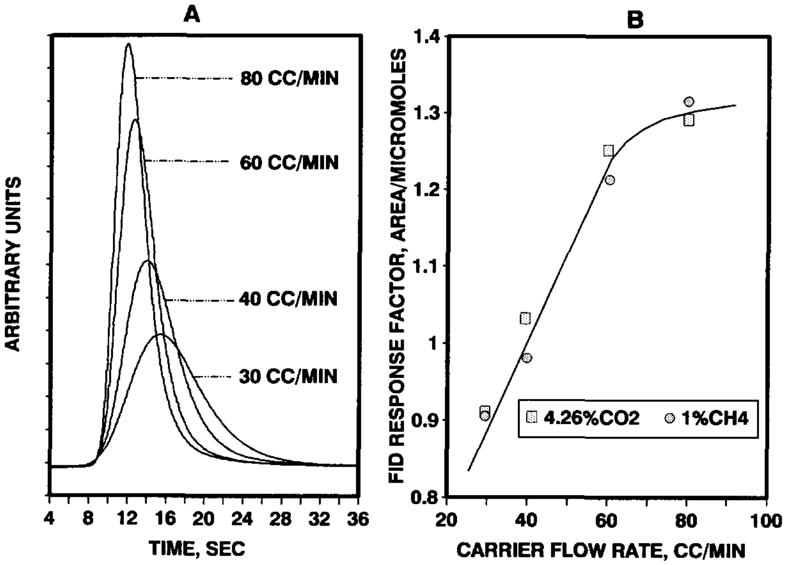

FIG. 5. Influence of carrier gas flow rate on FID sensitivity. (A) Hydrogenation of 4.26% CO_2 pulses at 673 K at various He carrier gas flow rates. (B) FID response factor as a function of He carrier gas flow rate of 1% CH_4 pulses and in the hydrogenation of 4.26% CO_2 pulses.

sensitivity of the FID depends strongly on the carrier gas flow rate and that the sensitivity increases with the flow rate linearly up to 60 cc/min and then it is leveled off at higher flow rates.

Application of the Technique

As was stated in the Introduction, one of the advantages of this modified TPO technique is its ability to monitor the carbon oxidation continuously. In Figure 6, a comparison between the present technique and the one using a GC column (to separate CO_2 and O_2) and a TCD is shown. The latter misses the peak temperature, peak height, and the fine structure. One can improve the spectrum quality of the latter technique by shortening the sampling interval as much as possible (minimum time required for CO_2, O_2, and H_2O elude from the column) and doing multiple runs.

Figure 7 shows the coke analysis of a reforming catalyst, containing 6 wt% of coke, using DTA. The DTA analyses were done using 1, 3, and 20% O_2 in nitrogen. In this DTA equipment and most of the others, carrier gas does not flow through the sample. The spectrum obtained with 1% O_2 shows that there are severe diffusional limitations. The TPO spectrum has no distinct feature and coke oxidation does not finish up to 1023 K. Though some improvement is observed when O_2 concentration is increased to 3%, its TPO spectrum is still devoid of well-defined peaks. When air is used, two distinct peaks appear in its TPO spectrum. At this high O_2 concentration the oxidation of coke is no longer limited by oxygen diffusion and is controlled by reaction kinetics. Comparing this spectrum with the one obtained with the present technique, it can be seen both spectra are similar, though the latter was obtained with 1% O_2. Besides an obvious shift of the DTA spectrum to lower temperatures with respect to the TPO spectrum because of higher O_2 concentration, the relative size of the first peak is bigger in the DTA spectrum than in the TPO. This means that heat evolved per unit of carbon in the oxidation of coke that corresponds to the first peak is larger than the one that corresponds to the second. It suggests that coke

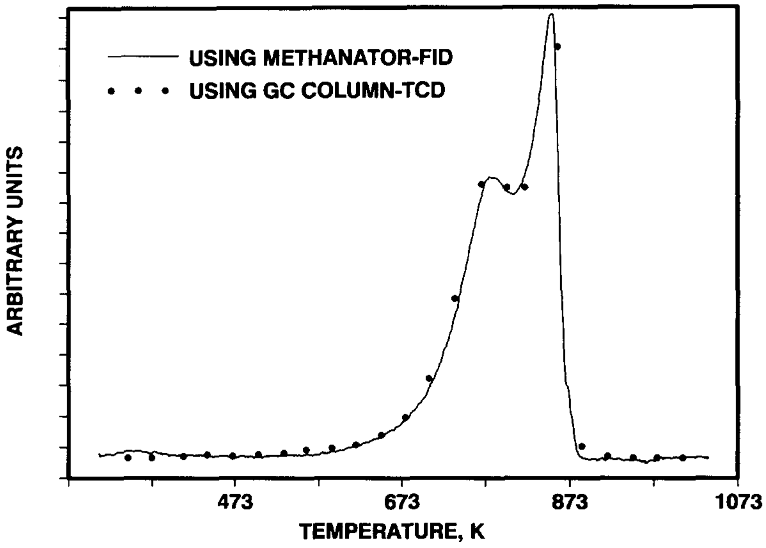

FIG. 6. Comparison of TPO spectrum obtained with a GC column-TCD and with a methanator-FID. Carrier gas, 1% O_2/He; carrier flow rate, 60 cc/min; heating rate, 13 K/min.

in the first peak contains more hydrogen than coke in the second peak.

Oxygen diffusion limitations were also observed in a TGA apparatus used in the study of coke catalysts. The same featureless spectra were obtained with low oxygen concentrations in the carrier gas (Fig. 8).

The high sensitivity of the present technique is showed in Fig. 9. The spectrum was obtained with 20 mg of a coked catalyst containing 0.3 wt% carbon. At this extremely low level of carbon, the spectral resolution is still excellent and with minimal noise in the signal.

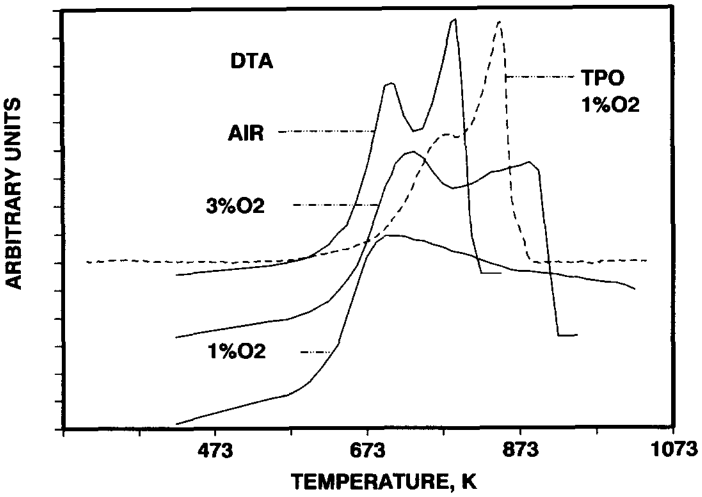

FIG. 7. Comparison of coke analysis obtained by DTA and TPO using methanator-FID. Carrier gas, 1% O_2/He in TPO; 1%, 3%, and air in DTA.

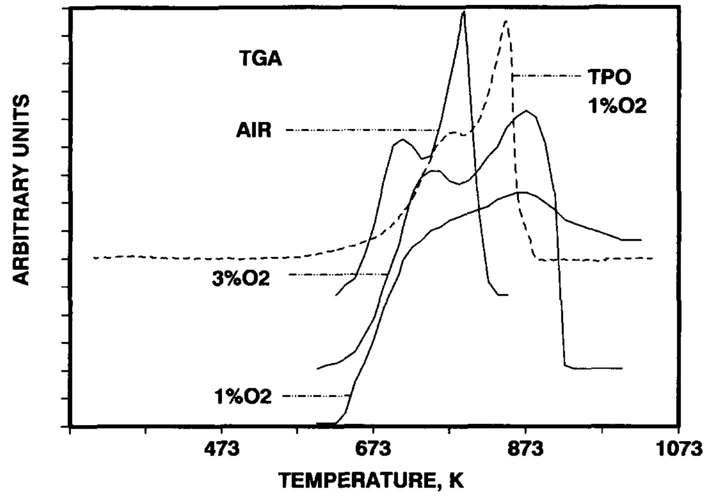

FIG. 8. Comparison of coke analysis obtained by TGA and TPO using methanator-FID. Carrier gas, 1% O_2/He in TPO; 1%, 3%, and air in TGA.

The continuous analyses makes it possible to differentiate clearly among cokes on various catalysts. Figure 10 shows the spectra of several coked catalysts used in various hydrocarbon processes: hydrogenation, reforming, fluid catalytic cracking, and methanol to olefins conversion. Amorphous carbon and graphite are also included. Some of them display symmetric peaks and the others show nonsymmetric peaks. It can be noted that even in the case of pure amorphous carbon, the peak is nonsymmetric. The peak temperature in the TPO spectra of the various coked catalysts strongly depends on the type of metal in the catalyst and on the type of coke deposits which are

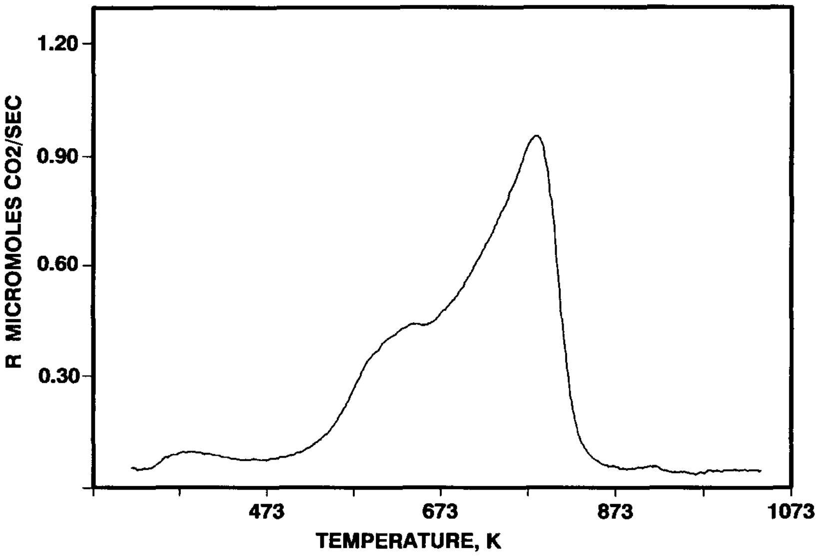

FIG. 9. TPO of coked reforming catalyst with 0.3% coke. Same conditions as in Fig. 6.

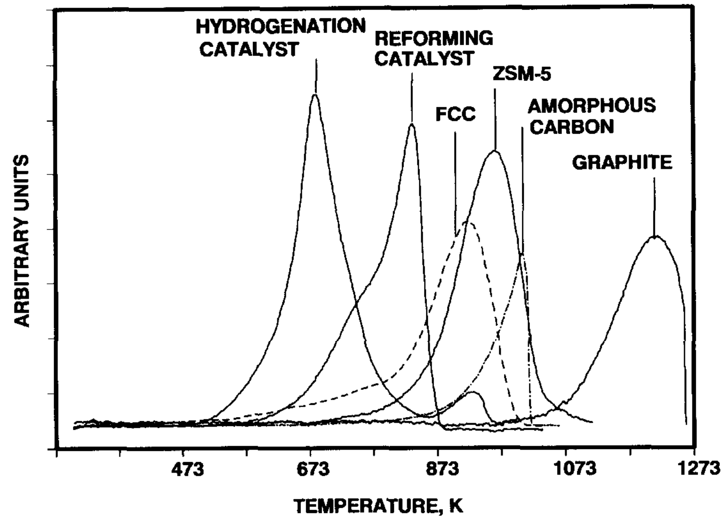

FIG. 10. TPO of various coked catalysts, amorphous carbon and graphite. Same conditions as in Fig. 6.

influenced by the processing conditions. It appears that with the same type of catalyst, the lower the coke deposition temperature, the lower the temperature required to burn it off.

Another very useful information that is possible to obtain with this unit is the amount of hydrocarbons that are released from the coked catalyst when it is heated up. If the gas stream coming out of the sample cell bypasses the methanator, the total amount of *hydrocarbons* (not CO_2 or CO) liberated from the catalyst can be monitored continuously by the FID. This can be done either using helium, hydrogen, oxygen, or any other carrier gas. When the gas stream goes through the methanator, the total amount of carbon liberated from the catalyst in the form of CO_2, CO, and unreacted hydrocarbon is measured. These experiments provide additional information about the characteristics of the coke deposit. Figure 11 shows the spectrum obtained when a coked reforming catalyst was heated in 10% H_2 in helium at 13 K/min up to 1023 K. The gas stream exited from the sample cell *went through the methanator*. The FID picked up a signal starting at 870 K and this signal was still increasing at the end of the temperature ramp. Since there is no oxygen in the carrier gas, it is reasonable to expect that the observed FID signal is due to hydrocarbon released from the catalyst via the reaction of hydrogen with coke. This expectation was proved to be wrong when the same experiment was run with a new sample of the same coked catalyst under the same conditions, except that the exit gas from the sample cell *bypassed the methanator* and went directly to the FID. If the previously observed FID signal is due to hydrocarbon releasing from the coke deposits one should observe the same FID signal. Figure 11 indicates that a much-reduced signal was observed when the methanator was bypassed, indicating that most of the carbon coming off from the coked catalyst under 10% H_2 is in the form of CO or CO_2 and only a small amount is in the form of hydrocarbon. Additional experiments have been carried out to understand how CO and CO_2 form in the absence of oxygen, and they will be published in a separate paper. One thing is certain, in the absence of gas-phase oxygen, the generation of CO, CO_2, and hydrocarbon from the coked catalyst occurs at very high temperatures, >823K.

Since a ruthenium catalyst is used to con-

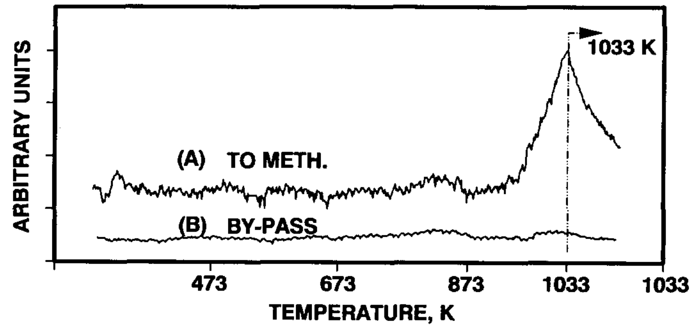

FIG. 11. Temperature programmed hydrogenation of a coked reforming catalyst. Carrier gas 10% H_2/He; flow rate, 60 cc/min; heating rate, 13 K/min. (A) Gas goes through methanator; (B) gas bypasses methanator.

vert CO_2 and CO to methane, deactivation of this catalyst through sulfur poisoning can occur. We have found that effective removal of sulfur contamination (as sulfur oxides) without removing CO_2 from the exit gas can be accomplished by installing a sulfur oxide trap in front of the methanator.

CONCLUSIONS

For the first time, a combination of methanator and flame ionization detector (FID) was used to monitor carbon oxidation rate in TPO of coked catalysts. Optimal experimental conditions have been defined for Ru/zeolite-13X in the complete conversion of CO_2 or CO to CH_4 in the presence of oxygen containing carrier gas. Oxygen affects the methanation efficiency of the Ru catalysts mainly through its conversion to water, which reduces the rates of CO_2 and CO hydrogenation to methane. Therefore, the higher the O_2 concentration, the higher the temperature and the lower the flow rate required to obtain complete conversion of CO_2 and CO. The upper limit in temperature is fixed by low equilibrium conversion encountered at high temperatures, as well as by the sintering temperature of the Ru catalyst. The lower limit for the flow rate is dictated by the sensitivity of the equipment and the mass-transfer limitation of oxygen. At very low mass flow rate of oxygen, oxygen concentration in the carrier gas drops to extremely low at temperatures where the carbon oxidation rate is appreciable. Under this condition the TPO measurement is not kinetically but diffusionally controlled by oxygen. An optimum concentration of O_2 and CO_2 exists for the quantitative conversion of CO_2 to CH_4 in the methanator. They are $<3\%$ and $<4\%$ for O_2 and CO_2, respectively. At higher CO_2 and O_2 concentrations, there is a thermodynamics limitation for the transformation of CO_2 into CH_4. When high oxygen concentration is desired, an oxygen trap should be installed in front of the methanator to quantitatively remove the oxygen without affecting the concentration of CO_2.

This technique has been proved to be very sensitive and useful in obtaining information about the characteristics of coke deposits. Other applications including analysis of low-level carbon contamination and selective chemisorption of carbon-containing species for metal dispersion and acidity measurements are being explored.

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