Advanced Temperature-Programmed Oxidation (TPO) of Coked Catalysts Using Integrated Methanation and FID Detection

1. Background

Heterogeneous catalysis is integral to a wide array of industrial applications, including energy, chemical synthesis, and consumer products. Traditionally, a solid or powder catalyst is employed to transform gas phase hydrocarbons into valuable products. Elemental carbon deposition onto the catalyst, or “coking,” is an undesirable side reaction that, over time, will block the catalytic sites and deactivate the catalyst. Therefore, characterization of carbon deposits is essential for improving catalyst performance. Today, advanced techniques such as transmission electron microscopy (TEM), laser Raman spectroscopy, electron energy loss spectroscopy (EELS), solid-state ^{13}C NMR, and temperature-programmed oxidation (TPO) are widely used to study coked catalysts. Among these, TPO has become one of the most commonly applied methods due to its simplicity and effectiveness.(1)

Temperature-programmed oxidation (TPO) is a materials characterization technique in which the sample is exposed to oxidizing gas, and the oxidizer chemically binds (chemisorbs) onto the surface. As the material temperature increases, the oxidized surface species desorb from the material and are analyzed by a detector. For coke analysis, the catalyst is heated under O_2 flow, and surface carbon is oxidized to CO_2. The amount of desorbed CO_2 is directly related to the amount of coke, and the temperature at which CO_2 desorbed can differentiate between types of carbon on the catalyst. Typically, the desorbed product is analyzed by a thermal conductivity detector (TCD) or flame ionization detector (FID), but neither detector is sufficiently sensitive to CO_2. Therefore, a methanation step can be employed to convert CO_2 into CH_4, which is easily measured by a flame ionization detector (FID). This process is shown in Figure 1.

This **AMI** Note discusses the use of TPO combined with an innovative detection method developed by Dr. S.C. Fung and Dr. C.A. Querini at Exxon Research and Engineering Company.(2) This approach is straightforward and enables continuous monitoring of the rate of coke oxidation. **AMI** is currently the only company to offer **customizable** catalyst characterization systems capable of such advanced TPO techniques.

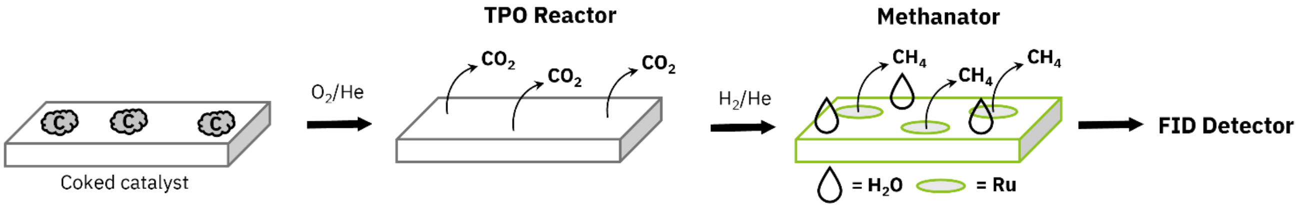

Figure 1: Step-by-step process for detection of coke through sequential temperature-programmed oxidation (TPO) and methanation using an ***AMI catalyst characterization system*** *equipped with a methanator and FID*

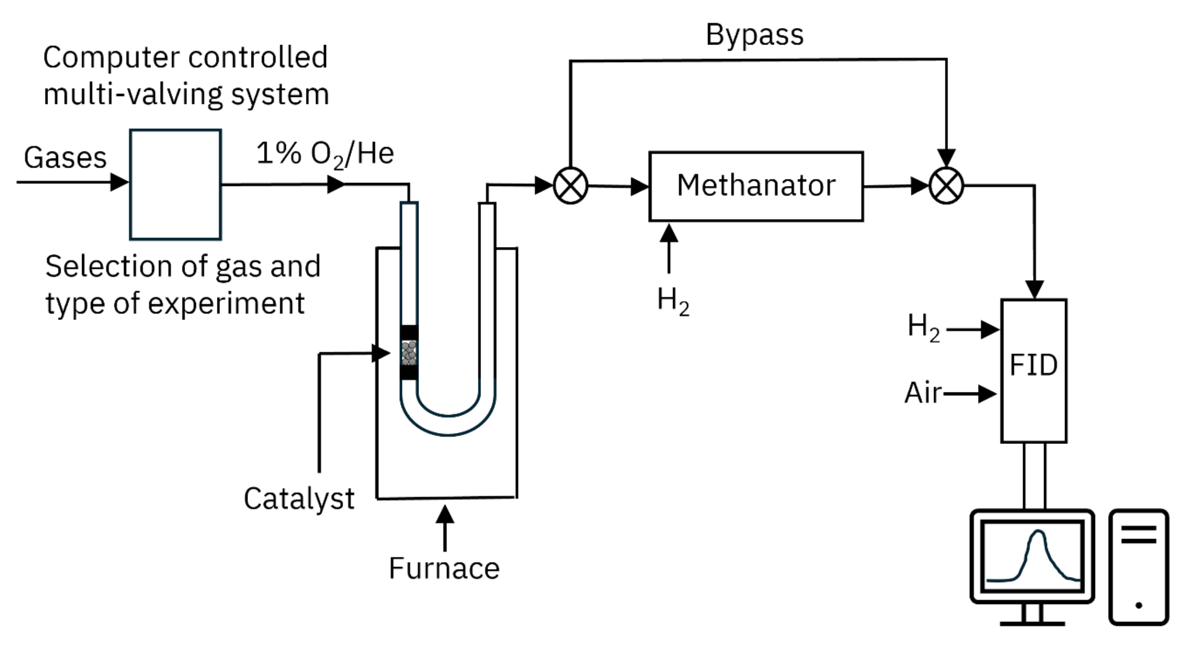

*Figure 2: System flow diagram for **AMI catalyst characterization system** equipped with temperature-programmed oxidation (TPO) flow reactor, methanator, and FID*

2. Experiment

In this TPO method, elemental carbon (coke) on the catalyst surface was oxidized to CO_2 by flowing O_2 through a temperature-controlled flow reactor. However, CO_2 is undetectable by an FID, so the CO_2 was flowed to a **methanator** and hydrogenated to CH_4. An **AMI catalyst characterization system** equipped with a methanator and FID was used for these experiments, and Figure 2 shows the system's flow diagram.

The methanator consisted of a small reactor filled with Ru catalyst positioned downstream of the sample U-tube. When hydrogen and CO_2 passed through the methanator, the Ru catalyst quantitatively hydrogenated CO_2 to CH_4, Therefore, the rate of CH_4 formation was assumed to be equivalent to the rate of coke oxidation. The CH_4 then flowed into the FID, which provided a real-time measurement of the coke oxidation rate. A GC column was unnecessary because the FID is insensitive to excess O_2 and water vapor in the gas stream.

	TPO Experiment	**Methanation Experiment**
Catalyst	~20 mg coked catalyst	~500 mg 40 wt% Ru/zeolite 13X
Reactant Gas	1% O_2/He, 20-80 mL/min flow rate	100% H_2, 22 mL/min flow rate
Temperature	Temperature increased linearly until complete oxidation achieved	Temperature ranged from 320 °C to 430 °C

Table 1: Experimental conditions for quantification of catalytic coke by TPO and methanation

The experimental details for the sequential TPO and methanation reactions are described in Table 1. Under these conditions, CO_2 was quantitatively converted to CH_4, while the excess O_2 in the carrier gas was reduced to H_2O. The combined gas stream then flowed directly into the FID.

3. Results

3.1 Influence of Oxygen Concentration

Since TPO experiments require an excess of oxygen, it was necessary to evaluate how oxygen concentration in the gas stream affects the methanation of CO_2 to establish optimal operating conditions. The effects of flow rate and methanator temperature on the hydrogenation efficiency of the Ru catalyst were also investigated, along with the impact of various pretreatments on the Ru catalyst's activity.

% CO_2 in Pulse	**% O_2 in He Carrier**			
	0	0.5	1	3
	% CO_2 Conversion to CH_4			
1	100	100	100	63
2	100	100	100	61
4.26	100	100	100	55

Table 2: Results showing percent CO_2 conversion to CH_4 at varying pulsed CO_2 and O_2 concentrations

To study the influence of oxygen concentration on CO_2 methanation, pulses of 1%, 2%, and 4.26% CO_2 in helium were introduced into the methanator with 0%, 0.5%, 1%, and 3% oxygen. As shown in Table 2:

- ✓ The CO_2 pulses were completely converted to CH_4 except when the oxygen concentration was increased to 3%.

3.2 Influence of Water Formation and Methanator Temperature

One possible explanation for this behavior is that water formed in the methanator (due to the oxygen present in the carrier gas) reduced the equilibrium conversion of CO_2 to CH_4 (Eqn. 1 and 2).(2)

$$1/2O_2 + H_2 \leftrightarrow H_2O \qquad (1)$$

$$CO_2 + 4H_2 \leftrightarrow 2CH_4 + 2H_2O \qquad (2)$$

Higher oxygen concentrations lead to greater water formation, which in turn affects the equilibrium conversion of CO_2 to CH_4. Table 3 shows:

- ✓ TPO experiments should be conducted with oxygen concentrations at or below 3% and at methanator temperatures below 430 °C to avoid equilibrium limitations.

However, the incomplete conversion of CO_2 to CH_4 observed in Tables 2 and 3 may depend on other factors besides equilibrium limitations.

% O_2	**1% CO_2 Pulse**			**4% CO_2 Pulse**		
	320 °C	400 °C	430 °C	320 °C	400 °C	430 °C
	% Equilibrium CO_2 Conversion					
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	99.26	90.06
10	99.74	86.00	66.45	78.00	49.70	37.32

Table 3: Results showing the influence on temperature on equilibrium CO_2 conversion to CH_4 at varying pulsed CO_2 and O_2 concentrations

% Gas in He Carrier	**Methanation Temperature (°C)**	**Carrier Gas Flow Rate (4.26% CO_2/He Pulse)**	
		60 mL/min	20 mL/min
		% CO_2 Conversion	
1% O_2	350	82	100
	400	100	100
3% O_2	400	55	100
2.6% H_2O	350	75	100
	400	100	-

Table 4: Results showing the relationship between carrier gas flow rate and CO_2 conversion at varying O_2/H_2O concentrations and methanation temperatures

3.3 Influence of O_2 Concentration, Methanator Temperature, and Flow Rate

An alternative explanation is that water inhibits the methanation activity of the ruthenium catalyst. To investigate this, experiments were conducted varying three parameters: the oxygen concentration in the carrier gas, the methanator temperature, and the carrier gas flow rate, and the results are shown in Table 4. At 350 °C, increasing the flow rate of 1%O_2/He to 60 mL/min resulted in 82% CO_2 conversion, while lowering the flow rate to 20 mL/min increased the CO_2 conversion to 100%. At 400 °C the flow rate was no longer limiting, and both 60 mL/min and 20 mL/min rates achieved total CO_2 conversion to CH_4. At higher O_2 concentrations (3% O_2/He), the same trend emerged with only 55% conversion to methane at high flow rates (60 mL/min). Lowering the flow rate to 20 mL/min brought the CO_2 conversion back to 100%. Therefore:

- ✓ Higher O_2 concentrations require lower flow rates to maintain CO_2 conversion.
  - ○ Higher O_2 concentrations produce more water, and lower flow rates are necessary to reduce the total number of water molecules at a given time.

Experiments were also conducted by introducing water directly into the methanator by saturating the carrier gas at room temperature, producing a 2.6% water concentration in He. This water level was comparable to that generated during oxidation in a 1.3% oxygen environment. A He pulse with 4.26% CO_2 was also introduced to the reactor. At 350 °C, the CO_2 conversion was largely unaffected by the water presence in the gas stream, showing 100% conversion to methane at lower flow rates (20 mL/min) and 75% conversion to methane at higher flow rates (60 mL/min). At 400 °C, the water-saturated CO_2/He reactant reached 100% conversion even at the higher, less optimal flow rate. These results confirmed previous findings that oxygen concentrations should ideally remain below 2%. For experiments requiring higher oxygen levels, an oxygen trap can be installed upstream of the methanator. These traps effectively remove oxygen without affecting the CO_2 concentration exiting the sample U-tube.

As indicated in Table 4, CO_2 conversion increased with both rising temperature and decreasing flow rate. This behavior suggests that conversion limitations in the presence of oxygen are primarily kinetic in nature. Additionally, the catalyst's activity improved with temperature. However, the methanator temperature should be kept as low as possible to minimize the risk of agglomeration of the ruthenium particles, which would permanently reduce catalyst activity.

3.4 Considering Detector Sensitivity

Experimental results indicated that FID sensitivity increased linearly with carrier gas flow rates up to 60 mL/min. At higher flow rates, the FID response plateaued, suggesting that flow rates above this level do not further improve sensitivity. The sensitivity of FID and TCD to methane were compared in Figure 3. While the experimental data overlapped, the FID results were much more precise than the TCD.

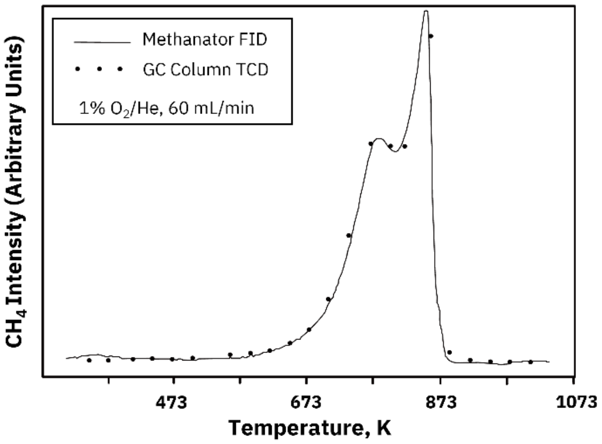

Figure 3: Plot comparing the sensitivity of CH_4 detection for two detectors: FID and TCD

3.5 Sulfur Poisoning

An additional important observation was the deactivation of the ruthenium catalyst in the methanator due to sulfur poisoning. This deactivation was caused by sulfur oxides generated during the combustion of sulfur-containing coke deposits. The most effective solution was the installation of a sulfur oxide trap upstream of the methanator, which successfully removed sulfur contaminants without affecting the CO_2 concentration.

4. Conclusions

These experiments demonstrate that TPO coupled with methanation and FID detection is a highly effective technique for monitoring the carbon oxidation rate of coked catalysts. By optimizing experimental parameters, complete conversion of CO_2 or CO to CH_4 is achievable, even in the presence of oxygen-containing carrier gases. This method is sensitive enough to detect carbon concentrations below 0.1% and can distinguish subtle variations in the coke distribution on catalyst surfaces.

AMI is the only company to offer chemisorption analyzer platforms that can be integrated with an FID detection system and methanation reactor for advanced TPO studies. The **AMI 300** and **AMI 400 Series chemisorption analyzers**, shown in Figure 4, are designed for customizability. **AMI**

chemisorption analyzers can easily be fitted with a methanator/FID module at the customer's request. This unique configuration enables precise, real-time quantification of coke oxidation rates with unparalleled sensitivity. This **AMI** Note summarizes a presentation delivered by Dr. S.C. Fung at an **AMI** (formally Altamira) U.S. User's Meeting. For further details on this TPO methodology, see (2).

5. References

(1) Herold, F.; Gläsel, J.; Etzold, B. J. M.; Rønning, M. Can temperature-programmed techniques provide the gold standard for carbon surface characterization? *Chem. Mater.* **2022**, *34*, 8490-8516.

(2) Fung, S. C. and Querini, C. A. A highly sensitive detection method for temperature programmed oxidation of coke deposits: Methanation of CO_2 in the presence of O_2. *J. Catal.* **1992**, *138*, 240-254.

Figure 4: ***AMI chemisorption analyzers*** *for catalyst characterization*