The measurement of small amounts of coke by a sensitive TGA/FTIR technique

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A useful, high-sensitivity method for quantifying small amounts of coke on a catalyst was developed. A TGA/FTIR technique was used. Gases evolved from the sample during the thermogravimetric analysis were transferred from the furnace by a purge gas to the flow cell of an FTIR. The intensity of the infrared spectra of evolved gases, such as CO_2, was measured as a function of time and displayed as a chromatogram. Integration of the chromatograms was compared to that of a standard sample and gave the amount of coke deposited on the catalyst. The carbon deposition on sulfated sol–gel zirconia in the isomerization of n-butane at 200 °C was measured. The carbon content was 0.013 wt% following deactivation for 15 min and 0.06 wt% after 180 min.

Keywords: carbon measurements, coke, FTIR, TGA, sulfated zirconia, isomerization, n-butane

Sulfated zirconia is known to be one of the most active solid acid catalysts for low-temperature hydrocarbon skeletal rearrangements [1–3]. However, its high initial activity decreases rapidly with time on stream reducing its usefulness in industrial applications [4–7]. Coke deposition has been proposed as one of several reasons responsible for the rapid deactivation of sulfated zirconia [8–13]. For this reason, it is of significance to understand the deactivation mechanism or mechanisms, especially the effect of coke formation. It was found that the amount of coke required to poison a sulfated zirconia catalyst was very small. Yori et al. reported [14] that the carbon content was 0.2 wt% on a catalyst which had been deactivated for about 4 h at 300 °C in the isomerization of n-butane measured by a combustion-volumetric method. Because the rapid decline in the catalytic activity of sulfated zirconia occurs in the first 15–90 min of reaction, it is necessary to find a method to measure the very low levels of coke formed in this time frame as precisely as possible.

Different techniques have been used to obtain quantitative information regarding the deposition of coke. For example, differential thermal analysis (DTA) [15] and thermal gravimetric analysis (TGA) [16] have been used in an effort to quantify coke formation. Using a methanator to convert CO_2 into methane, Fung and Querini [17] were able to measure carbon contents as low as 0.3 wt%. A method which made use of a mass spectrometer had a detection limit of 0.03 wt%, but had a rather poor resolution at this low carbon content [18]. Using a TGA/Quadrupole MS [19], we identified the presence of carbon on deactivated sulfated zirconia. However, due to instrumentation sensitivity limitations and, also, due to the fact that the weight loss was not solely due to the selective removal of carbon, this technique was not capable of obtaining precise carbon measurements.

It is well known that infrared is very sensitive to CO_2 because of its high extinction coefficient [20]. For this reason, a TGA/FTIR technique was developed in our laboratory to measure the CO_2 evolved during thermal analysis. Using this technique, we have been able to make some precise measurements of the coke required to poison the sites responsible for the deactivation of sulfated zirconia [21].

In this TGA/FTIR technique, a thermogravimetric analyzer (TGA 2950, TA Instruments, Inc.) was coupled to a Fourier transform infrared spectrometer equipped with a gas cell, commonly referred to as a light pipe (Bruker IFS 55). The infrared spectrometer includes a sensitive, liquid-nitrogen-cooled, mercury–cadmium–telluride (MCT) detector. Gases evolved from the sample during the thermogravimetric analysis (TGA) were transferred from the furnace by a purge gas into the flow cell of the infrared spectrometer. Approximately 35 mg of sample were placed on the TGA balance and a purge gas at a rate of 70 ml/min was used to transfer the gases from the TGA unit into the infrared spectrometer. The interface was maintained at 200 °C to avoid condensation of the gases evolved. A temperature program from room temperature to 1000 °C at a temperature ramp rate of 20 °C/min was used. Spectral resolution was 4 cm^{-1} with 16 single scans coadded in a time frame of approximately 2 s to obtain each spectral file. Depending on the experimental requirements, N_2, O_2, or He (all UHP grade, Doussan) was used as the purge gas, which was dried using a gas purifier (AllTech). The TGA furnace was cleaned prior to each run by heating to 1050 °C for 0.5 h. The system was under continuous purge in order to maintain a stable and consistent background for each purge gas. Compressed air (zero grade, Doussan) was also used as a

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purge gas in some cases to study the regeneration of deactivated sulfated zirconia. However, for carbon detection, air is not recommended as a purge gas, because impurities such as CO_2 may interfere with the results.

A spectroscopic software, the OPUS/Chrom package (version 2.0, Bruker Instruments, Inc.), was used for the measurement of the time-dependent TGA/FTIR data. As a result of a measurement with the OPUS/Chrom package, a sequence of spectra were recorded in constant time intervals. The intensity changes in the spectra were measured as a function of time and stored as so-called chromatograms. These chromatograms were derived by integration over spectral regions of interest. All measured spectra and the chromatograms were stored in a single file, the so-called chrom-file. Four spectral regions were selected: 3986–3790 cm^{-1}, the O–H stretching region (H_2O); 2143–2000 cm^{-1}, the C–O stretching region (CO); 2392–2250 cm^{-1}, the O–C–O asymmetrical stretching region (CO_2), and 1420–1300 cm^{-1}, the O–S–O asymmetrical stretching region (SO_2). The infrared absorbance was calculated across each of the spectral regions to produce four separate chromatograms which correspond to H_2O, CO, CO_2, and SO_2, respectively. Depending on the species of interest, different spectral regions can be integrated to give information of species evolved from the catalyst [22].

Calcium oxalate monohydrate ($CaC_2O_4{\cdot}H_2O$) (Spectroscopic grade, Fisher Scientific) was used as a standard. The reason for this choice is that it shows three distinct weight losses due to the evolution of H_2O, CO, and CO_2, respectively. The observed weight losses are shown in figure 1 as a function of temperature. The first derivative of the weight losses has also been included in figure 1. The purge gas used in the decomposition was N_2. The decomposition equations are [23]:

$$CaC_2O_4{\cdot}H_2O \rightleftharpoons CaC_2O_4 + H_2O \quad (\sim 177\,^{\circ}C,\ \text{first weight loss})$$

$$CaC_2O_4 \rightleftharpoons CaCO_3 + CO \quad (\sim 515\,^{\circ}C,\ \text{second weight loss})$$

$$CaCO_3 \rightleftharpoons CaO + CO_2 \quad (\sim 754\,^{\circ}C,\ \text{third weight loss})$$

The temperatures correspond to the maxima of the weight-loss peaks, as shown from the first-derivative weight-loss curve. The infrared chromatograms corresponding to this decomposition under N_2 flow are shown in figure 2. This data was obtained using the TGA interface with the FTIR as previously described. The gases evolved have peaks in the same position as shown in figure 1. However, because the intensities are a function of both the amount of gas evolved and the corresponding infrared extinction coefficients, the integrated areas under each peak are quite different. It is important to point out that, in the evolution of CO, a portion of this CO disproportionates to form carbon and CO_2. This CO_2 appears as a low-temperature feature in the CO_2 chromatogram. The relatively large intensity of this feature is due to the very large extinction coefficient of CO_2 relative to that of CO.

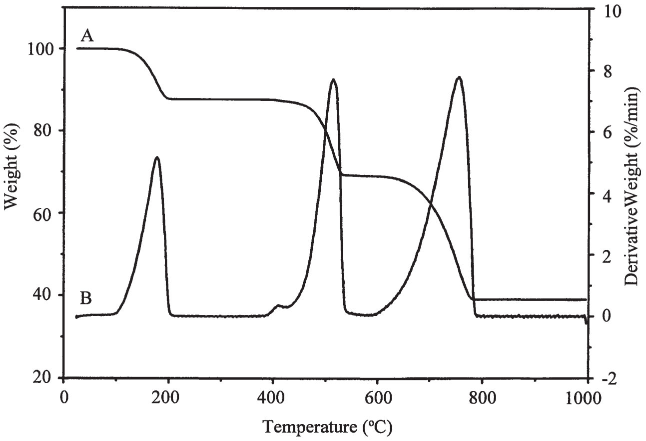

Figure 1. The TGA weight losses of calcium oxalate monohydrate. Curve (A) stands for the percent weight loss, (B) the first derivative of the weight loss.

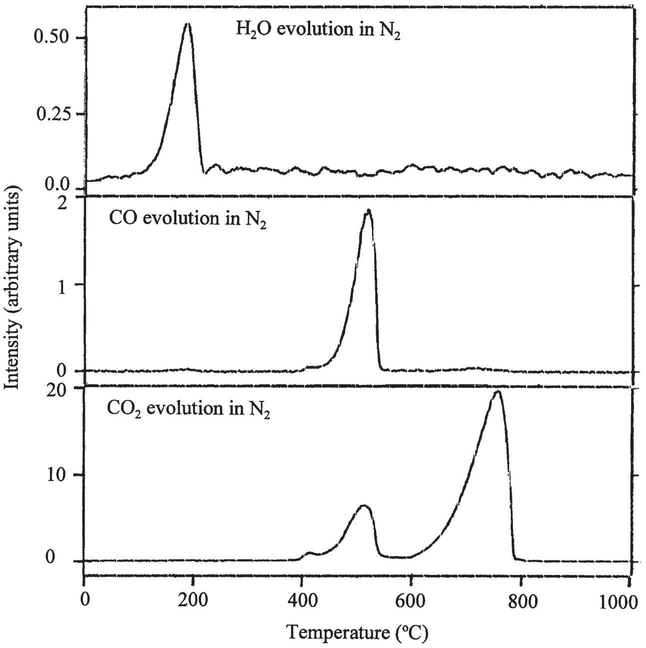

Figure 2. The chromatograms of gases evolved from calcium oxalate monohydrate obtained by TGA/FTIR in N_2 flow.

Integrated band intensities for CO_2, CO, and H_2O are as follows [24]: CO_2 (2349 cm^{-1} band), 2700 $cm^{-2}\,atm^{-1}$, CO (2143 cm^{-1} band), 260 $cm^{-2}\,atm^{-1}$, and H_2O (3755 cm^{-1} band), 100 $cm^{-2}\,atm^{-1}$. Only the high-temperature CO_2 feature should be used as a calibration standard for carbon. The CO_2 evolved at the lower temperature is the result of a secondary reaction which involves CO and not the primary decomposition reaction [25]. The CO_2-integrated areas (arbitrary units) are shown in table 1. The average of two runs (entries 1 and 2 in table 1) is 307.355 area/mg of $CaC_2O_4{\cdot}H_2O$. The experimental error between the two runs is 0.03%. Since 1 mg of $CaC_2O_4{\cdot}H_2O$ contains 0.082 mg of carbon which contributes to the evolution of CO_2 (second peak only), the calculated calibration factor is 3739.5 area/mg of carbon.

Table 1
The integrated areas of the evolution of CO_2 from calcium oxalate monohydrate obtained by TGA/FTIR.

Entry	Purge gas	Initial sample weight (mg)	Integrated area of CO_2 evolution	Area of CO_2/mg of $CaC_2O_4 \cdot H_2O$
1	N_2	15.062	4630	307.40
2	N_2	15.307	4704	307.31
3	O_2	14.535	4897	336.91
4	O_2	14.743	4909	332.97

Table 2
Carbon deposition on sulfated sol–gel zirconia in the isomerization of n-butane at 200 °C.

Time on stream (min)	Conversion of n-butane (%)	Carbon (wt%)
15	41.41	0.013
45	6.36	0.024
90	1.41	0.034
180	0.73	0.062

The CO_2 evolved from a deactivated sulfated zirconia is shown in figure 3(A). The intensity scales used are different from those in figure 1. The sulfated zirconia was prepared using a two-step sol–gel method [25]. It had been deactivated in the isomerization of n-butane over a period of 3 h at 200 °C. The TGA/FTIR experiment was performed using N_2 as the purge gas. The integrated area under the CO_2 peak was 81 using the same intensity scales as in the calcium oxalate. Using the standard area/mg of carbon, 81 was calculated to be equivalent to 0.02166 mg of carbon. The sample weight was 35 mg. Therefore, the carbon content on the catalyst was determined to be 0.062 wt%. Similarly, carbon contents of catalysts deactivated for different times were obtained and are shown in table 2. The high sensitivity of the TGA/FTIR is apparent from the results shown in table 2. It is possible to detect carbon contents as low as 0.01 wt% (100 ppm) on a 35 mg sample. The experimental error is estimated to be less than 2%. This error is introduced primarily as a result of the state of dehydration of the sample in the initial weighing. Table 2 shows the very low tolerance of sulfated zirconia with respect to carbon formation. When the coke deposited reached 0.04 wt% (90 min reaction time), the catalytic isomerization activity was reduced to 10% of its initial value. The atomic carbon to sulfur ratio was detailed in a separate paper [21]. As an example, a carbon to total sulfur ratio of 1 : 15 was determined following deactivation for 180 min. However, since the active sulfur was only about 10% of the total sulfur, the carbon to active sulfur ratio was only 1 : 2.

Under N_2 flow, carbon atoms deposited on the active surface sites of sulfated zirconia react with oxygen atoms from sulfate groups on the surface to form CO_2. The original reason as to why N_2 was used as a purge gas in the study of sulfated zirconia was to obtain information regarding the relationship between specific surface sulfur species and coke [26].

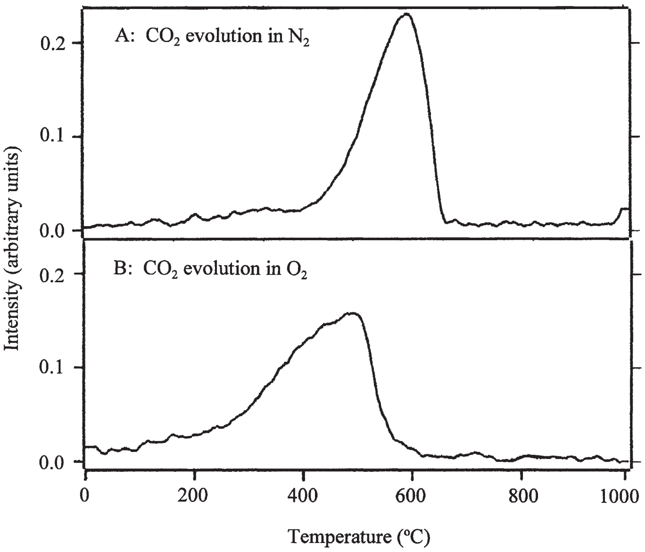

Figure 3. The chromatograms of CO_2 evolved from deactivated sulfated zirconia obtained by TGA/FTIR. (A) With N_2 purge, (B) with O_2 purge. The catalyst was deactivated in the isomerization of n-butane at 200 °C for 3 h.

In general, temperature-programmed oxidation is more widely used in coking studies. TGA/FTIR experiments were performed on standard $CaC_2O_4 \cdot H_2O$ and sulfated zirconia using O_2 as a purge gas. The results of the $CaC_2O_4 \cdot H_2O$ decomposition experiment in an oxygen flow are included in table 1 (entries 3 and 4). The integrated area/mg of carbon was 4084.64. The CO_2 chromatogram over sulfated zirconia in an oxygen flow is shown in figure 3(B). The integrated area under the CO_2 peak was 89. Calculation using these calibrations resulted in a carbon content of 0.062 wt%, identical to that obtained under N_2 flow.

In conclusion, the TGA/FTIR technique is simple, highly sensitive and useful in obtaining precise information regarding the deposition of small amounts of coke on catalysts.

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References

[1] M. Misono and T. Okuhara, Chemtech (November 1993) 23.
[2] X. Song and A. Sayari, Catal. Rev. Sci. Eng. 38 (1996) 329.
[3] T. Yamaguchi, Appl. Catal. 61 (1990) 1.
[4] A. Corma, M.I. Juan-Rajadell, J.M. Lopez Nieto, A. Martinez and C. Martinez, Appl. Catal. 111 (1994) 175.
[5] J.E. Tabora and R.J. Davis, J. Chem. Soc. Faraday Trans. 91 (1995) 1825.
[6] G. Larsen, E. Lotero, R.D. Parra, L.M. Petkovic, H.S. Silva and S. Raghavan, Appl. Catal. 130 (1995) 213.
[7] T. Cheung, J.L. D'Itri and B.C. Gates, J. Catal. 151 (1995) 464.
[8] J.R. Sohn and H.W. Kim, J. Mol. Catal. 52 (1989) 361.

[9] F.R. Chen, G. Coudurier, J.-F. Joly and J.C. Vedrine, J. Catal. 143 (1993) 616.
[10] T.T.Ng. Flora and H. Norbert, Appl. Catal. 123 (1995) L197.
[11] C. Li and P.C. Stair, Catal. Lett. 36 (1996) 119.
[12] M.R. Gonzalez, K.B. Fogash, J.M. Kobe and J.A. Dumesic, Catal. Today 33 (1997) 303.
[13] D. Spielbauer, G.A.H. Mekhemer, E. Bosch and H. Knözinger, Catal. Lett. 36 (1996) 59.
[14] J.C. Yori, J.C. Luy and J.M. Parera, Appl. Catal. 46 (1989) 103.
[15] J.M. Parera, R.J. Verderone, C.L. Pieck and E.M. Traffano, Appl. Catal. 23 (1986) 15.
[16] J. Biswass, P.G. Gray and D.D. Do, Appl. Catal. 32 (1987) 371.
[17] S.C. Fung and C.A. Querini, J. Catal. 138 (1992) 240.
[18] S.M. Augustine, G.N. Alameddin and W.M.H. Sachtler, J. Catal. 115 (1989) 217.
[19] B. Li and R.D. Gonzalez, Ind. Eng. Chem. Res. 35 (1996) 3141.
[20] N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy* (Academic Press, New York, 1964).
[21] B. Li and R.D. Gonzalez, Appl. Catal., in press.
[22] P.R. Griffiths and J.A. de Haseth, *Fourier Transform Infrared Spectroscopy* (Wiley, New York, 1986).
[23] G.D. Parks, *Mellor's Modern Inorganic Chemistry* (Wiley, New York, 1967).
[24] S.S. Penner, *Quantitative Molecular Spectroscopy and Gas Sensitivities* (Addison Wesley, London, 1959) p. 23.
[25] D.A.C. Compton, M. Markelov, M.L. Mittleman and J.G. Grasselli, Appl. Spectroscopy 39 (1985) 909.
[26] B. Li and R.D. Gonzalez, Appl. Catal. 165 (1997) 291.