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Coke characterization by temperature programmed techniques

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Abstract

The use of a temperature programmed (TP) technique in coke characterization is discussed. Oxygen is one of the gases most often used in the TP technique (TPO) to infer coke types and coke locations on the catalyst. Additional information about the morphology of the coke deposits can be obtained when TPO is coupled with a kinetic model. This is because coke deposits with a tridimensional structure exhibit a coke reaction order increasing from close to 0 to approaching 1 as the oxidation reaction proceeds. The change in the coke reaction order can be observed with a properly designed partial burn TPO experiment. When the TP technique is used with an inert gas (TPI), one expects any product being generated would be hydrocarbon molecules. However, gasification of coke deposits to CO and CO_2 was observed in the absence of external oxygen. It has been found that the oxidation products are the results of a direct reaction of the alumina surface hydroxyl groups with the coke deposits. Because of this, the maximum amount of coke that can be eliminated corresponds to the amount of hydroxyl groups on the alumina surface.

Keywords: Coke characterization; Temperature programmed technique; Partial burning; Oxygen; Catalyst deactivation

1. Introduction

Catalyst deactivation by coke deposition is an important fact in petrochemical and petroleum industries, both from an economics and technological point of view. The loss of catalyst activity due to the accumulation of coke deposits makes it necessary either to stop the unit to regenerate the catalyst, or to adopt different technologies such as alternately swinging out a reactor from the reactor train for regeneration or with continuous regeneration of the catalyst moving from reaction to regeneration zones.

The regeneration of coked catalysts often involves several steps. In supported metal catalysts, regeneration is complicated by metal sintering during coke oxidation, and therefore a redispersion and reduction step must be carried out.

In order to optimize catalyst regeneration, information regarding coke burning kinetics should be obtained. Coke characterization is also needed because the location and the structure of coke greatly influence the coke burn kinetics especially when metal promoters are present. Several techniques have been used to study the carbonaceous residues, e.g., FTIR [1,2], TEM [3–5], laser Raman spectroscopy [6], EELS [7], ^{13}C-NMR [8], Auger electron spectroscopy and secondary ion mass spectrometry [9], small-angle neutron scattering [10], etc. All these techniques give different types of information on coke composition, structure and location, but no information on the reactivity and behavior of coke regarding to thermal

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treatments. The most widely used technique for this purpose is the temperature programmed technique. It has been used to characterize coke in several catalytic systems, such as reforming catalysts [11–16], zeolites [17], Ni catalysts [18,19], etc. Oxygen diluted with various inert gases is often used in temperature programmed oxidation of coke, but H_2 [20,21] and CO_2 [21] have also been tried.

Classical configurations in performing a TPO experiment include detection systems such as: TCD to measure CO_2 in a gas chromatographic system, or its measurement with a mass spectrometer, differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) equipment. Recently, we reported a new detection system for TPO. This detection system greatly increases the sensitivity and resolution [22]. 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. With this technique it is possible to quantify carbon on catalysts as low as 0.01 wt%. This modification also improves the stability of the baseline, and therefore it is especially useful when kinetics parameters must be obtained from TPO experiments. Recently we have published a discussion of the power-law kinetic model [23] for the coke–O_2 reaction. By using a linear combination of power-law kinetic expressions, it was possible to study the influence of heating rate, coke concentration, coke particle size and number, catalyst mass and oxygen concentration on TPO spectra.

At the end of a normal reforming operation, the coke level is often as high as 14% [24]. It has been shown that at high levels of coke, coke-free areas of the support still exist [25]. Therefore, coke is organized on the support in tridimensional particles. This has been confirmed by TEM [3] and with several characterization techniques by Espinat et al. [26]. They indicated that at low coke level, small stacks of aromatic ring structures less than 10 Å in size are deposited. Then these carbonaceous units gather to form porous large carbon particles as coke level increases. Since this tridimensional structure influences the kinetics of the coke–O_2 reaction, by changing the coke reaction order and the pre-exponential factor, it is important in the development of a kinetic model to have such information.

In this paper we discuss two useful techniques, though not commonly employed, in temperature programmed experiments to characterize coke deposits. The first is the use of partial burning experiments to obtain information about the structure of coke. The other topic deals with the study of the interaction of coke with the alumina support of naphtha reforming catalysts, by using temperature programmed gasification technique in an inert carrier gas.

2. Experimental

Temperature programmed gasification experiments were carried out in a modified AMI-1 unit, manufactured by Altamira Instruments. In a typical temperature programmed experiment, the carrier gas at constant flow rate of 60 cm^3/min is fed into the sample cell under ambient conditions. The sample temperature is increased linearly at the desired heating rate of 13°C/min from room temperature to a given final temperature at which the coke deposits are completely removed. In a partial burn experiment, the sample temperature is raised to an intermediate value and stays at this temperature for a fixed period of time such as 30 min. This does not allow complete removal of coke deposits but provides valuable information about coke morphology. The exit gas is fed into a methanator which is supplied with a pure hydrogen stream at 22 cm^3/min. A supported Ru catalyst in the methanator quantitatively transforms CO_2 and CO into CH_4, which is continuously monitored by a flame ionization detector (FID). This method greatly improves the sensitivity, the stability of the baseline and the resolution of the conventional temperature programmed technique. Additional details of this procedure can be found elsewhere [22]. Experiments using different carrier gases have been carried out, e.g., pure helium, 10% H_2 in helium, helium saturated with water and 1% O_2/He.

Temperature programmed experiments have also been carried out using a mass spectrometer, to detect H_2, CO, CO_2 and water. In these experiments, the heating rate was 5°C/min and the flow rate 50 cm^3/min.

Coked catalysts were generated by exposure to *n*-heptane. Pt–Re/Al_2O_3 and Pt–Re–S/Al_2O_3 catalysts were coked at 525 kPa, 500°C for 213 h, and Pt/Al_2O_3

was coked at 1225 kPa, 482°C for 290 h. The mathematical model used to obtain kinetic parameters for the reaction between coke and oxygen, and to simulate the partial burn experiments has been described in detail in Ref. [23].

3. Results and discussion

3.1. Coke morphology characterization

Fig. 1A shows the TPO of a Pt–Re/Al_2O_3 catalyst containing 4.11% C, a Pt/Al_2O_3 catalyst containing 1.24% C and a Pt–Re–S/Al_2O_3 catalyst containing 13.0% C. Fig. 1B shows results of partial burning experiments carried out with these catalysts, heating from room temperature to 450°C, 490°C and 500°C, for Pt/Al_2O_3, Pt–Re/Al_2O_3 and Pt–Re–S/Al_2O_3, respectively. The partial burn experiments were continued at the above temperatures for 30–40 min. Despite the much higher levels of coke deposited on the Pt–Re and Pt–Re–S catalysts as compared to the Pt catalyst their TPO spectra are similar. However, the partial burn experiments show very distinct features for these catalysts. With the Pt catalyst, after a final temperature of 450°C was reached, the rate of CO_2 production monotonically decreases. On the other hand, Pt–Re catalyst which has a higher coke level shows a faster decrease in the CO_2 production rate after some time (t_c) at constant temperature. This effect is more pronounced with the heavily coked Pt–Re–S catalyst. This should not occur if a power-law kinetic expression with constant coke reaction order is assumed for the reaction between coke and oxygen. For a constant carbon reaction order of 1, an exponential decay in the rate of CO_2 formation with time should occur at constant temperature because coke conversion varies exponentially with time for a first order reaction. This is what was observed with the Pt catalyst. For a constant carbon reaction order less than 1, the CO_2 formation rate decreases proportionally with time raised to a power of greater than 1. This CO_2 decay rate is slower than the exponential decay obtained when carbon reaction order is 1. The shapes of the constant temperature part of the TPO spectra in Fig. 1B for Pt–Re and Pt–Re–S do not agree with these two situations. However, the faster decrease in the CO_2 production rate after t_c can be explained by considering the change in coke reaction order. If initially, coke is present as tridimensional particles on the catalyst surface, coke reaction order is lower than 1 and can be close to 0 if the coke particles are very large. We have previously reported a coke reaction order of 0.77 in the TPO experiment of supported Pt catalyst [23] and Hughes et al. obtained a coke reaction order of 0.75 from their coke burn data [27]. Large tridimensional coke particles have been observed by TEM at high coke level [3], therefore, coke reaction order is expected to increase from less than 1 to close to 1 during the coke burn process as coke particles decrease in size. This is because reaction rate in a gas–solid reaction is proportional to the solid surface area. The surface area of large coke particles changes very slowly with loss of coke at the early part of burning, because similar surface areas are being generated due to a very slow decrease in particle diameters. When a substantial amount of coke is burned off, the coke reaction order becomes 1. This occurs when all carbon atoms are exposed and, therefore, available to react with oxygen. In this case, particles are very small or coke is present as a monolayer on the catalyst surface. Fig. 2 shows the partial burn simulations of a single type of carbon, where coke reaction order increases as coke content decreases. In these cases, curves very similar to those experimentally observed for Pt–Re and Pt–Re–S are obtained. It is possible to observe an increase in the rate of decay of CO_2 production, which is more pronounced when sudden changes in reaction order

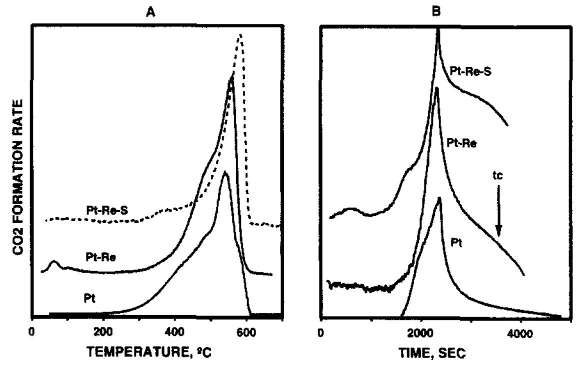

Fig. 1. (A) TPO for Pt–Re/Al_2O_3, Pt/Al_2O_3 and Pt–Re–S/Al_2O_3 catalysts, (B) partial burn experiments: heating up to 450°C for Pt, 490°C for Pt–Re and 500°C for Pt–Re–S. t_c indicates time at which an acceleration of the rate of decay of CO_2 production occurs.

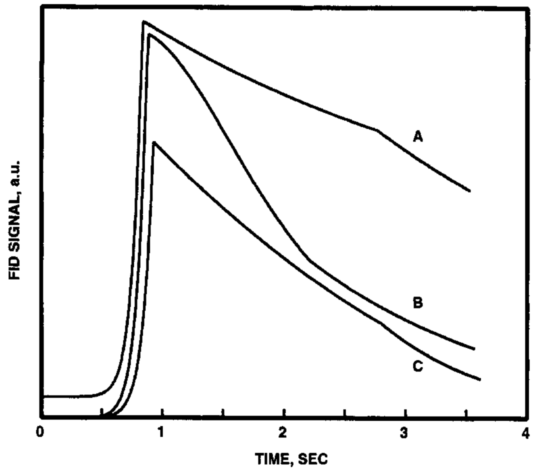

Fig. 2. TPO spectra simulation of partial burning experiments, with coke reaction order changing as a function of coke content, 3 wt% C on catalyst. (A) coke reaction order=0 for C>1.8%, order=1 for C<1.8%; (B) order=0.2 at 3% C and then increasing linearly up to 1, when C=1.8%. (C) order=0.7 for C>0.6%, order=1 for C<0.6.

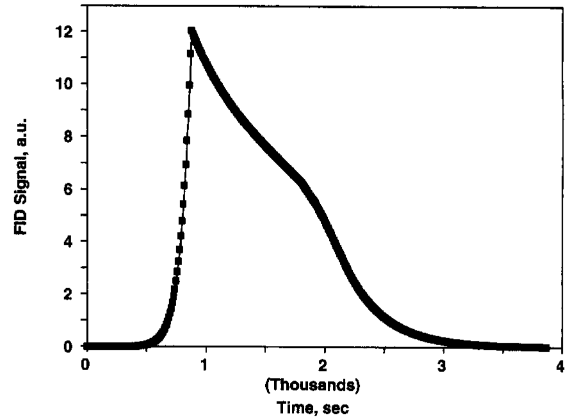

Fig. 3. A simulation spectrum of a partial burning experiment for coke reaction order changes as a function of coke content. Initial coke content 8.5%, divided among six different particle sizes with two morphologies represents by: 1% C, constant order of 1; five fractions of 1.5% C each, initial order 0.3 and final order 1, order changes at conversion levels of 0.8, 0.82, 0.83, 0.84 and 0.85 for the five fractions, respectively.

occur, such as in curves A and C, where a change in reaction order from 0 to 1 and 0.7 to 1 occurs at a given coke content. The larger the difference in the reaction order, the more difference in the CO_2 decay rate at t_c. These simulations show a discontinuity in the first derivative of the CO_2 production curve. However, experimental results do not show such a feature (Fig. 1B). This might be due to the fact that initially there is a distribution of particle sizes and different particle morphologies, and because of this, a smooth transition zone is observed when the coke reaction order changes from values smaller than 1 to 1. Fig. 3 shows a simulation with consideration to the variations in initial particle size and geometry. It is remarkable that this simulated spectrum looks so much like the spectra of the Pt–Re and Pt–Re–S catalysts in Fig. 1B. It is not possible to simulate the shape of the partial burn curves of Pt–Re and Pt–Re–S with a constant coke reaction order even when several types of coke deposits are considered in the simulation. Therefore, this type of partial burning experiments could be used to obtain additional information about the coke morphology, so that one can decide if change in reaction order should be considered in the deconvolution of the TPO spectrum in obtaining parameters for heavily coked catalysts.

3.2. *Coke gasification using an inert carrier gas*

Fig. 4 shows the results of TPO and stripping experiments using helium (TPHe) and 10% H_2 in helium (TPH), on a Pt–Re/Al_2O_3 catalyst with 1.2% C. All experiments were carried out at a heating rate of 13°C/min and with a carrier gas flow rate of 60 cc/min. The stripping experiment with helium surprisingly

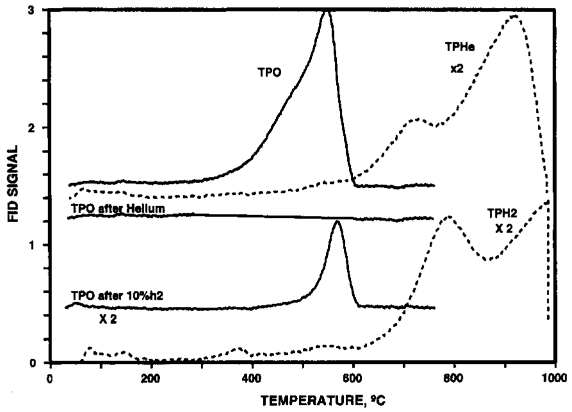

Fig. 4. TPO, TPHe and TPH of a Pt–Re/Al_2O_3 catalyst. Initial coke content: 1.2%; carrier gas flow rate: 60 cc/min; heating rate: 13°C/min. Carrier gas: TPO, 1% O_2/He; TPHe, pure He; TPH, 10% H_2/He.

removed all the coke, though it required substantially higher temperatures than those in TPO. Two peaks were observed in the TPHe spectrum at 730°C and 920°C. The final temperature in the TPHe experiment was 1000°C. TPO performed after the helium stripping experiment showed that there was no coke left after the TPHe. It is even more astonishing that stripping with 10% H_2/He, under the same conditions, removed less coke from the catalyst than with pure helium (Fig. 4). TPO carried out after the TPH experiment indicates that TPH failed to remove all coke deposits, suggesting that hydrogen has an inhibiting effect and slows down the reaction occurring during TPHe. Because of this, both peaks in the TPH spectrum move to higher temperatures as compared with those in TPHe.

Fig. 5 shows the results of a consecutive helium stripping experiment which was carried out up to 900°C and was quickly cooled down to room temperature. In this case, not all coke was removed in the first TPHe, but it was totally eliminated in the second TPHe. The third TPHe and the final TPO show that there was no coke left after the second TPHe. Although the first TPHe ended at 900°C, there was coke burn signal starting at as low as 600°C in the second TPHe. This suggests that the second peak (the 900°C peak) in the TPHe spectrum in Fig. 4 is indeed a very broad peak with a starting coke gasification temperature at close to 600°C. This broad peak is not composed of two or more peaks in the temperature range from 600°C to 1000°C. If this would have been the case the lower temperature coke would be completely removed and only some of the high temperature (900°C peak) coke deposit could be remaining after the first TPHe. Therefore, the coke gasification in the second TPHe would occur at temperatures much higher than 600°C.

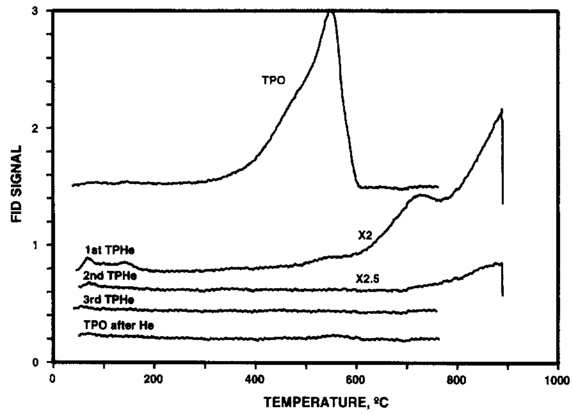

Fig. 5. Consecutive TPHe of a Pt–Re/Al_2O_3 catalyst, initial coke content 1.2%. Same conditions as in Fig. 3.

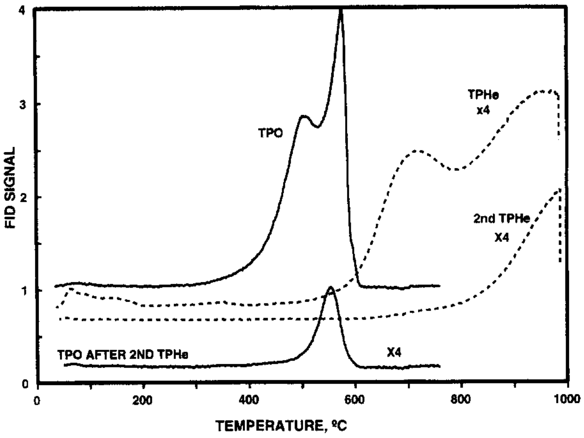

Fig. 6. TPO and TPHe of a Pt/Al_2O_3 catalyst containing 8.5% coke. Two consecutive TPHe were carried out up to 900°C.

A catalyst with higher coke content was also used in the TPHe experiments. Results obtained with a 0.6 wt% Pt/Al_2O_3 having 8.5% coke are shown in Fig. 6. In this case two consecutive TPHe were carried out up to 1000°C. However, not all coke was gasified from this catalyst, as shown in the final TPO. These results indicate that when increasing the amount of coke on the catalyst, it is not possible to gasify all the coke using an inert gas.

A possible explanation to these results is that the catalyst support plays an important role in this process. A series of experiments was carried out using wet helium (0.6% H_2O), or running the TPHe with a mixture of 3/1 alumina to coked catalyst (particle size 60–80 mesh). Another TPHe experiment was carried out with gases coming out of the sample cell bypassing the methanator. In this case, any FID signal observed is due to hydrocarbons being released during the thermal treatment, since conversion of CO and CO_2 to CH_4 is not possible without the methanator. Fig. 7 shows the results of this series of experiments, on a Pt–Re/Al_2O_3 catalyst containing 2% coke. It can be seen that the presence of water gives a small increase in the amount of coke being gasified. There is little effect on coke gasification of adding pure alumina to the coked catalyst. When the methanator

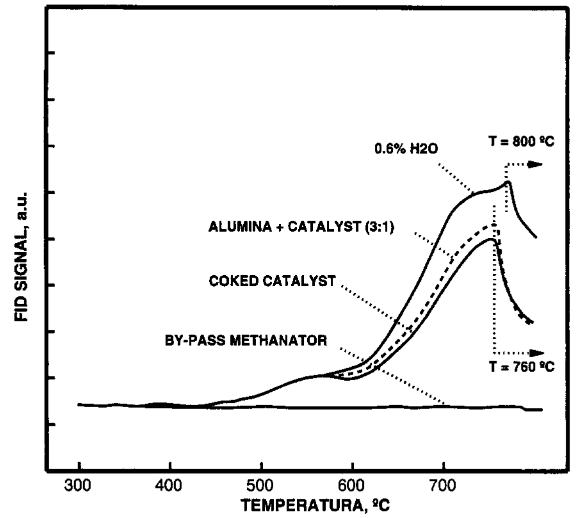

Fig. 7. TPHe experiments with a Pt–Re/Al_2O_3 catalyst containing 2% coke.

was by-passed no signal was observed, indicating that no hydrocarbons are released from these catalysts upon heating in helium. This was confirmed by using a mass spectrometer. Two consecutive TPHe were carried out with the mass spectrometer scanning at a mass range of CO, CO_2, H_2O and H_2 (results not shown). Water release occurs only at low temperature, while hydrogen and CO increase significantly above 500°C. The second TPHe showed that hydrogen in the gas phase was less than the first TPHe.

Helium carrier gas at a purity level of 99.999% was further purified by passing it through a Chrompack oxygen filter to reduce oxygen concentration to below 1 ppm. Therefore, impurities in helium should not be an issue in the gasification of coke in the TPHe experiments. This belief is further strengthened by TPHe experiments carried out with C60 and amorphous carbon (results not shown). No gasification of C60 (contains essentially no oxygen) was detected and only a very small amount of the active carbon was gasified. When the same carbon loading was used in the TPHe experiments, the amorphous carbon produced a signal less than 5% of the coked catalyst. The gasification of the amorphous carbon is mainly due to the removal of oxygenated groups from the amorphous carbon.

It appears that reaction between water, liberated by the dehydroxylation of Al_2O_3 at high temperature, with the coke deposits may be the reason why coke can be gasified under a helium stream. The total amount of water coming from the hydroxyl groups can be estimated from the weight of the coked catalyst and the number of hydroxyl groups per gram of alumina. The number of hydroxyl groups on the surface of alumina depends upon the temperature used in its preparation [28]. At moderate calcination temperatures the number of OH groups are 12.6×10^{14} cm^{-2}. For an alumina support with a surface area of 200 m^2/g, the hydroxyl group is estimated to be 2.5×10^{21} OH/g. In a typical TPHe experiment, about 0.01 g of coked catalyst was used. Since two hydroxyl groups result in one water molecule from dehydroxylation of alumina, the total amount of water generated, in cc of gas at room temperature and atmospheric pressure, is 0.51 cc. This amount of water was liberated in a period of 25 min in which gasification was observed (assuming there is no water liberation at the low temperature region when there is no FID signal). If we assume water is liberated at a constant rate within the 25 min period, the time average water concentration in the helium carrier gas, flowing at 60 cc/min at ambient condition is calculated to be 0.034%. The addition of alumina in the amount of three times that of the coked catalyst essentially has little impact on the gasification rate indicating coke gasification by water liberated from the dehydroxylation of the Al_2O_3 hydroxyl groups does not proceed to a significant extent. Similarly, the addition of 0.6% of H_2O (about 20 times the amount would be generated by dehydroxylation of the catalyst) into the He carrier stream shows only a small effect on the gasification rate indicating the direct reaction of water with the coke deposits is slow.

The most probable reaction mechanism is the direct reaction of coke with the Al_2O_3 hydroxyl groups, generating CO and H_2. If all of these groups are used to react with coke, to produce CO and H_2, the maximum amount of coke that could be removed is 5% based on the hydroxyl group concentration mentioned earlier. This might be the reason why the coke was completely removed from the low coke content catalyst, and it was not possible from the catalyst containing 8.5% coke. It also explains why hydrogen, a known gasification agent, when it is added to helium, is less effective in gasifying the coke deposits because the direct reaction of OH groups with coke deposits (reaction products CO, CO_2 and H_2) is inhibited by its product hydrogen. Under our reaction condition, coke gasification by hydrogen is considerably slower than the reaction between coke and OH groups as indicated by the lack of methane in the product stream in the TPH experiments reported by us previously [22]. The major reaction product is CO_x, and therefore, in the presence of hydrogen, gasification of coke to CO_x by the OH groups is still the dominant reaction though its reaction rate is attenuated by the added hydrogen.

4. Conclusions

Temperature programmed techniques were applied to two different problems. In the first one, it was shown that with a proper design of experiments, it is possible to obtain information about the morphology of the coke that otherwise requires the use of highly sophisticated techniques. Obviously, the partial burn technique by itself is not able to define precisely the coke particle size and geometry. However, their effect on the TPO and the partial burn TPO spectra can be simulated by a power rate law kinetic model, which provides a physical basis to interpret the experimental results.

In the second example, the gasification of coke on an Al_2O_3 support under an inert gas was found to be a property of the oxide support. The combination of TPHe, TPHe with water or hydrogen and TPO made it possible to establish that the reactive species are the hydroxyl groups on the surface of Al_2O_3. The limit in the amount of coke gasified is set by the number of the hydroxyl groups and has been determined to be 5–6%.

One of the major advantages of the FID detection method used in this technique is its high sensitivity and resolution, the latter being a consequence of the continuous signal obtained during the analysis, which makes it possible to observe all the distinct features of a temperature programmed analysis.

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