

REGENERATION OF DEACTIVATED β -ZEOLITE BY COKE OXIDATION

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Abstract

An accurate description of coke burn off is obtained from a catalyst based on β -zeolite and used for benzene alkylation with propylene giving cumene by using the thermogravimetric technique.

A simple empirical kinetic model was successfully applied to interpolate the data of thermogravimetric analysis performed on samples after partial burn off.

Different temperatures, partial pressures of oxygen and gas flow rates were the variables studied in order to calculate the apparent rates and the activation energy for the coke oxidation reaction and to outline the best conditions for the industrial regeneration procedure of our proprietary catalyst PBE-1 for cumene synthesis. Combining the unusually long lifetime per reaction cycle with the optimized regeneration procedure leads to an outstanding overall catalyst life.

Keywords: β -zeolite, coke, cumene, kinetics, regeneration, TG

Introduction

Coke formation is an undesirable side phenomenon associated with the transformation of organic compounds over heterogeneous catalysts, since it determines their deactivation. Deactivation by coke formation is reversible: removal of coke by an optimized regeneration process generally allows to recover the activity of the catalysts. For this purpose burning of coke is one of the most widely exploited methods.

To define a correct regeneration procedure several typical problems must be focussed. For example, structural or surface damages of the catalyst, generally associated with high temperature spots must be avoided. Coke oxidation is, in fact, a very exothermic reaction, involving water formation, that often irreversibly modifies the catalysts. Also coke transformations, during the treatment, must be taken into account: condensation and aromatization reactions may lead to the formation of compounds more difficult to oxidize.

Thermal analysis represents an excellent tool to evaluate quantity and nature of coke and to study how to achieve the best regeneration procedure. In our laboratory several catalysts regeneration procedures have been successfully defined with the

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help of thermogravimetry. A prominent example is represented by a β -zeolite based catalyst [1], used for benzene alkylation with propylene giving cumene [2].

β -zeolite is a well known large pore, high silica zeolite which is hydrothermally synthesized in the presence of TEOH (tetraethylammoniumhydroxide) as template molecule. Although its synthesis was described for the first time in a patent filed in 1964 [3], its structure was resolved only 20 years later [4] and no industrial applications were developed for a long time.

Recently the catalyst has been successfully applied to industrial cumene production in our plant in Porto Torres (Sardinia) [5]. The catalyst under industrial operation is showing an extremely long lifetime. Due to the high cycle length, it is anticipated that catalyst regeneration would not be requested. In addition the optimized regeneration procedure here described would allow in any case to perform several reaction regeneration cycles without loss of performance. We studied a sample, coked in a pilot plant under accelerated reaction conditions and characterized by a moderate coke loading (5%).

We carried out a series of partial burn isothermal treatments of the sample in a microreactor at atmospheric pressure, with a large stoichiometric excess of oxygen in comparison with the coke, performed at several temperatures and several partial pressures of oxygen.

All the samples coming from the treatments were analyzed by TG performed at standard oxidative conditions.

The thermogravimetric data were elaborated with help of simple model to define kinetics and activation energy of the oxidation reaction.

Experimental

The catalyst sample was divided in several homogeneous portions of 50 mg. Each of them was treated in a quartz microreactor under different isothermal oxidative conditions, as reported in Table 1, at increasing times of isothermal treatment, in order to achieve an increasing degree of coke removal. In such a way each single run (1 to 10) is constituted of 4 to 7 partial burn experiments, characterized by different isothermal treatment times.

The oxidative gas mixture was prepared by means of two thermal mass flow controllers (Brooks Instruments). Adjusting the flow rates of oxygen and helium allowed to obtain the desired oxygen partial pressure and GHSV (Gas Hourly Space Velocity expressed as cm^3 of total gas volume in reaction conditions fed in 1 h divided by the volume in cm^3 of the catalyst (bulk density = 0.5 g cm^{-3})).

The approach to isothermal treatment conditions is done by increasing the sample temperature at constant rate (2°C min^{-1}) in the preheated oxidizing mixture by means of a controlled furnace (Micromeritics). Utilizing such a procedure we never observed thermal spots on the catalyst by the thermocouple near the sample.

Some experiments were also performed in an inert atmosphere to compare these data with those taken in oxidative atmosphere. In Table 2 the treatment conditions performed in inert gas are reported.

Table 1 Experimental conditions of isothermal treatments in oxidative atmosphere

Number of run	Temperature/ $^{\circ}\text{C}$	GHSV/ h^{-1}	Oxygen molar fraction
1	400	38100	0.176
2	400	38100	0.022
3	450	41000	0.022
4	450	41000	0.044
5	400	38100	0.044
6	350	35300	0.176
7	450	41000	0.176
8	500	43800	0.022
9	400	19100	0.176
10	400	76200	0.176

The coke content of all the samples coming from the treatments was determined by means of a thermogravimetric apparatus (Mettler TA3000). The analyses of about 20 mg of ground catalyst were performed in air ($30 \text{ Ncm}^3 \text{ min}^{-1}$) with a heating rate of $4^{\circ}\text{C min}^{-1}$ from room temperature to 850°C . An adsorption bed of molecular sieves (Zander MS-TE) was used to completely remove water and CO_2 from the air flowing into the TG or DTA instruments. The TG curves were normalized on the mass value determined at 620°C . So this value refers to the mass of catalyst after complete removal of water (both physisorbed and structural) and coke. The numerical integration of the DTG (derivative curve obtained from normalized TG) in the temperature range $300\text{--}620^{\circ}\text{C}$ represents the coke amount per gram of catalyst as defined before (C). The start value of coke content (C_0) is determined at the beginning of the isothermal conditions (and so at time of isothermal treatment equal to zero).

Table 2 Experimental conditions of isothermal treatments in inert gas

Number of run	Temperature/ $^{\circ}\text{C}$	GHSV/ h^{-1}
11	400	38100
12	450	41000
13	500	43800

The DTA signal was measured only on the coked sample. The analysis was performed in a NETZSCH ST 409 apparatus. 200 mg of sample were loaded on the balance and the analysis was carried out in air ($150 \text{ Ncm}^3 \text{ min}^{-1}$) with a heating rate of $4^{\circ}\text{C min}^{-1}$ from room temperature to 850°C . The reference sample was 200 mg of α -alumina.

Results and discussion

In Fig. 1 the DTG curves of the samples treated in a microreactor under oxidative conditions of run 2 (curves 2 to 5) together with that one of the untreated sample (curve 1) and of the fresh catalyst (curve 6) are reported. Particularly, curve 2 relates to the sample at isothermal treatment time equal to 0 min. i.e. just heated up to 400°C (see experimental part).

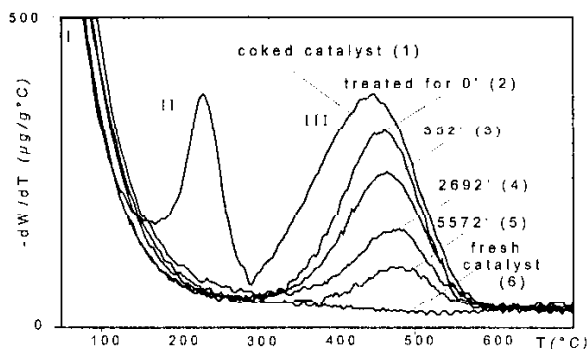


Fig. 1 DTG normalized curves of samples of run 2, treated at increasing isothermal time in a flow microreactor (curves 2 to 5), coked sample (curve 1), fresh catalyst (curve 6). The isothermal reaction times are respectively: 0, 352, 2692, 5572 min for curves 2–5

DTG curve 1 in Fig. 1, associated with unreported DTA experiments, evidences three well defined peaks in the temperature ranges:

(I) Room temperature to 150°C: evaporation of physisorbed water by an endothermic phenomenon.

(II) 150–290°C: oxidation of physisorbed light reaction products (oligomers), characterized by an exothermic DTA peak (we can not exclude that an endothermic evaporation is hidden under the global DTA exothermic peak).

(III) 290–600°C: coke oxidation characterized by a DTA exothermic phenomenon.

The first peak (room temperature–150°C) is always present on all samples owing to exposure to wet atmosphere before the TG analysis.

The compounds which constitute the second peak (range 150–290°C) are easy to be removed from the catalyst and disappear during increasing temperature as evidenced in curve 2 in Fig. 1.

The same curve also shows that the coke peak (range 290–600°C) decreases during this step, pointing out that a partial coke elimination occurs.

In inert gas we observe the same amount of residual coke also after prolonged treatment at different temperatures (400–500°C). This means that coke composition ranges from lighter to heavier moieties, the lighter one is eliminable without oxidative treatment.

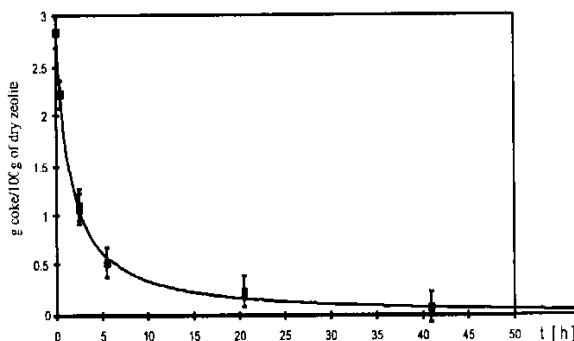


Fig. 2 Experimental data of run 7 and interpolated curve (Eq. 1) at $T=450^{\circ}\text{C}$, O_2 molar fraction=0.176 and $\text{GHSV}=41000\text{ h}^{-1}$

In oxidative conditions the amount of residual coke decreases as a function of the isothermal treatment time (curves 2 to 5 in Fig. 1). The slight shift, towards higher temperatures, of the maximum of the third DTG peak, may confirm the various composition of coke and its progressive enrichment in compounds more difficult to oxidize. At the same time, since the end temperature of oxidation TG step is equal to all the treated samples (600°C) we can say that no new species of coke were formed.

In Fig. 2 the data of coke content for run 7 are reported, determined and calculated as previously described. The interpolation curve is described by the Eq. (1):

$$C = C_0 \left[1 + (n-1)ktC_0^{n-1} \right]^{-1/(n-1)} \quad (1)$$

where C are grams of coke per gram of catalyst at treatment isothermal time t , C_0 are grams of coke per gram of catalyst at treatment isothermal time $t=0$, t is the time of isothermal treatment (s), n is the reaction order, k is the apparent rate constant (s^{-1})

Equation (1) is obtained from the integration between C_0 and C and between 0 and t of the Eq. (2) that expresses the coke oxidation rate [6]:

$$-\frac{dC}{dt} = kC^n \quad (2)$$

or, since oxygen flow is in large stoichiometric excess

$$-\frac{dC}{dt} = KC^n(Y_{\text{O}_2})^m \quad (3)$$

where

$$k = K(Y_{\text{O}_2})^m \quad (4)$$

This simple model fits very well all the experimental data giving a n value not far from 2 (1.7–2.3) for each experimental run.

Setting $n=2$ and recalculating the parameter k the values listed in Table 3 are obtained.

Table 3 As Table 1 with the apparent rate constant k obtained from Eq. (1) taking $n=2$ and the correspondent Σ least squares

Run	$T/^\circ\text{C}$	O_2 molar fraction	GHSV/ h^{-1}	k/s^{-1}	Σ least squares
6	350	0.176	35300	1.38E-6	0.03
2	400	0.022	38100	2.29E-6	0.29
5	400	0.044	38100	3.90E-6	0.11
1	400	0.176	38100	1.15E-5	0.02
10	400	0.176	76200	1.06E-5	0.16
9	400	0.176	19100	9.31E-6	0.09
3	450	0.022	41000	1.12E-5	0.05
4	450	0.044	41000	2.00E-5	0.73
7	450	0.176	41000	6.69E-5	0.01
8	500	0.022	43800	1.03E-4	0.26

The small difference among the apparent k of runs 1, 9, 10 pointed out that k is not significantly influenced by the flow rate of oxidizing gas (GHSV).

From the elaboration of runs 1, 2, 5 (400°C) and 3, 4, 7 (450°C) at different partial pressures we can estimate the m parameter from Eq. (4), setting the K value as only temperature dependent.

Table 4 Absolute rate constant K and m parameter as estimated from Eq. (4) from runs performed at same temperature with different molar fraction of oxygen

$T/^\circ\text{C}$	m	$K/\text{atm}^{-m} \text{s}^{-1}$
400	0.90	6.78E-5
450	0.86	3.00E-4

As follows from Table 4, the m parameters for the two runs are very close.

Taking an average m value of 0.88 the rate constants K at 350 and 500°C can be calculated (Table 5):

Table 5 Absolute rate constant K calculated from Eq. (4). m =average of values of Table 4

$T/^\circ\text{C}$	m	$K/\text{atm}^{-m} \text{s}^{-1}$
350	0.88	6.35E-6
500	0.88	2.96E-3

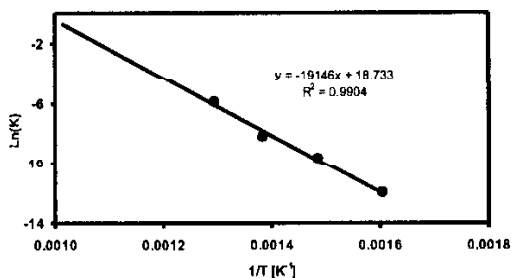


Fig. 3 Arrhenius plot

Utilizing these data the Arrhenius plot in Fig. 3 is drawn out. The apparent activation energy obtained is 159 kJ mol^{-1} . This value is very close to that of carbon burn off (about 155 kJ mol^{-1} [7]).

Conclusions

A kinetic study of coke burn off was made by means of TG that came out as a rapid and useful method.

The organic compounds present on our coked catalyst were completely removed with an oxidizing treatment.

Lighter compounds were desorbed at low-temperature also in inert atmosphere.

The kinetic study of oxidizing conditions allowed us to determine the apparent absolute rate constants (K) at different temperatures and partial pressures.

The calculated E_a (159 kJ mol^{-1}) is very close to that of carbon burn off (about 155 kJ mol^{-1}). It can be concluded that, in our experimental conditions, the reaction rate is substantially not diffusion controlled.

The model allowed to define an optimized industrial regeneration procedure of our proprietary PBE-1 catalyst for cumene synthesis. In such a way the high catalyst lifetime already shown during each reaction cycle is further extended.

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