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TG AND DSC STUDY OF THE PROPERTIES OF COKED MOLECULAR SIEVE CATALYST

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Abstract

A cracking catalyst designated *SRNY* was manufactured from a commercial *SRNY* molecular sieve (*M.S.*). The support consisted of kaolin, clay and SiO_2. The coking behaviour of the *SRNY M.S.*, the support and the catalyst were examined with light diesel oil (*LDO*) as feedstock in a microreactor. The physico-chemical properties of both fresh and aged samples, subjected to or not subjected to the cracking reaction of *LDO*, were sequentially characterized by means of pore structure determination and thermal analysis. The pore structure included the specific surface area and the pore volume or porosity. Thermal analysis methods used included TG and DSC.

The results indicated that all coked samples exhibited obvious changes in surface pore structure and acidity in comparison with non-coked samples. Their specific surface area and acid amount decreased with increase in the coke content of the samples. The apparent activation energy data obtained from decoking samples in an air flow, using the temperature-programmed oxidation (*TPO*) method, showed that the kinetic parameters of the *SRNY M.S.* differed from those of the *SRNY* catalyst and its support.

Keywords: acidity, activation energy, catalyst, DSC, pore structure, TG

Introduction

Catalyst coking, also called fouling, is one of the reasons for various catalyst deactivations; this phenomenon is caused by precursors originating from the reactants themselves. Owing to its importance in catalysis processes, it has led investigators to pay considerable attention to this interesting phenomenon in the catalysis field. Hughes [1], Petersen *et al.* [2] and Butt *et al.* [3] discussed in detail the problems concerned with catalyst deactivation in petrochemical processes in their monographs, in which they also introduced a series of methods for examining coke formation and the coking mechanism. The methods used were microscopic observation, X-ray diffraction analysis, pore structure BET determination and tests of chemical reactivity.

The main purpose of the present paper is to examine some properties of the solid samples before and after coking by using thermal analysis methods (e.g.

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TG and DSC), which are regarded as essential methods to measure coke content, to characterize acidity and to determine the activation energy of a solid sample (molecular sieve, support or catalyst) in addition to the determination of its pore structure.

The experimental results indicated that coke was formed on the inner and outer surfaces and pore walls of the solid samples and mainly in the fine pores, and that the acid amount of *SRNY M.S.* was the greatest for the three kinds of samples, and its effect on coke deposition was most serious. The results obtained from the burning coke test showed that the average enthalpy of coke combustion was quantitatively related to the coke content, and the apparent activation energies of coke combustion on various samples differed from one another.

Experimental

Sample preparation

a. *SRNY M.S.* was developed by the Research Institute of Petroleum Processing and produced by the Changlin Petrochemical Factory. The *SRNY M.S.* was washed with distilled water according to a conventional method for catalyst preparation.

b. The catalyst support was provided from the Research Institute of the Changlin Petrochemical Factory and consisted of kaolin, clay and SiO_2.

c. The catalyst *SRNY* was a mixture of *SRNY M.S.* and support, and the ratio of the *SRNT M.S.* to the support was 30 to 70 (mass%).

According to a conventional procedure, portions of the three samples mentioned above were steamed at 800°C for 4 h.

The data from physicochemical analysis of the given samples are listed in Table 1.

Table 1 Data obtained from physico-chemical analysis of solid samples

Sample		*SRNY M.S.*		*SRNY* catalyst		Support	
Condition		fresh	aged	fresh	aged	fresh	aged
Chemical composition mass /%	Na_2O	0.27	0.43	<0.03	<0.03	0.43	0.51
	Fe_2O_3	0.09	0.09	0.27	0.30	0.36	0.41
	SO_4^{2-}	1.41	–	0.96	0.60	0.60	–
	RE_2O_3	5.2	–	1.6	–	–	–
	Al_2O_3	15.87	17.57	35.89	39.10	43.40	52.90
SiO_2/Al_2O_3 ratio		6.26	12.92	7.35	15.7	–	–

Determination of surface pore structures of samples

The specific surface area and pore volume of the samples before and after coking were measured with a low-temperature N_2 adsorber of ASAP-2400 type from Micromeritics, U.S.A.

Coke deposition and burning off coke for samples

a. Coke deposition

Coke was deposited on a WFS-1A micro-reaction system, which consists of a MRCS-03 microreactor and SP-2305 GC device, with *LDO* as feedstock. The experimental conditions were as follows: amount of sample 5.0 g, amount of feed oil 1.56±0.2 g, reaction temperature 460°C, stream time 70 s, *WHS* 16 h^{-1} and catalyst/oil ratio 3.2 (m). It is necessary to state here that we studied only the changes in certain properties of the samples before and after coking, but the results concerned with the microactivity (*M.A.*) and selectivity of given samples in *LDO* microreaction experiments are not discussed in this paper.

b. Coke burning off experiment

The coke burning off experiment was carried out on the thermogravimetry (TG) module of a DuPont 9900 Computer/Thermal Analysis System with the following test conditions: oxygen pressure 0.01 MPa, flow rate 100 $ml \cdot min^{-1}$, isothermal time at 340°C 60 min, and heating rate 10 $deg \cdot min^{-1}$ form 340 to 600°C.

The coke content was calculated by deducting the loss of water from the total loss in mass of the sample in the experiment in the temperature range from 340 to 600°C. This method, generally called the *TPO* procedure, is similar to that described in Ref. [4].

Acidity measurements on samples

The acidity of the samples was measured by an in situ *TPD* method on TG with NH_3 adsorption–desorption. Details of the operation are to be found in ref. [5].

Measurements of kinetic parameters and enthalpy of coke burning

The coke of samples was burnt off by means of the differential scanning calorimeter (DSC) module of the DuPont 9900 Computer/Thermal Analysis System and the kinetic parameters (apparent activation energy and preexponential factor) and the enthalpy of coke combustion were calculated from the DSC curve by Kissinger's peak temperature method (*PTM*) [6]. The detailed operatdetailed operating procedure is as follows: the non-coked sample (ca. 10 mg) was put in a DSC reference cell, while the coked sample to be tested (ca. 10 mg) was put in another DSC cell (called the sample cell); the oxygen pressure was 0.01 MPa, the flow rate was 50 ml·min^{-1} and the isothermal time at 340°C was 30 min; the heating rate was 5, 10 or 20 deg·min^{-1}, from 340 to 650°C.

The experimental programme was conducted according to computer instructions, and the computer automatically recorded the DSC scanning curve and stored the data on disks.

When an experiment was finished, the data were analysed according to the Kissinger formula, and the activation energy and preexponential factor were calculated from the data stored on the disks.

The Kissinger formula is as follows:

$$\ln(\beta/T_p^2)=\ln(R/E)+\ln A-E/RT_p$$

where β=heating rate (deg·min^{-1}), T_p=peak temperature in DSC curve (°C or K), E=activation energy (J·mol^{-1}), A=preexponential factor (min^{-1}) and R=universal gas constant (J·deg^{-1}·mol^{-1}).

Then, the average enthalpy of coke combustion of the sample (ΔH, J·g^{-1}) was obtained by integrating the peak area of the DSC curve.

Results and discussion

Coke content deposited on sample

The data on the coke contents of the samples measured by TG are listed in Table 2.

Table 2 Results on coke contents of samples

Sample	*SRNY M.S.* aged at / °C				*SRNY* catalyst aged at / °C		Support aged at / °C	
Condition	fresh	800	800	800	fresh	800	fresh	800
		2 h	4 h	8 h		4 h		4 h
Coke content, m%	7.08	3.24	2.67	1.96	2.55	0.89*	0.65*	0.49

* data measured by SB-3 instrument

The data in Table 2 demonstrate that the level of coke deposition on *SRNY M.S.* is greater than that on the catalyst and support, when *LDO* is used as feedstock under the given experimental condition for microreaction operation. Though the *SRNY M.S.* is only one-third by mass in the catalyst, the coke content of fresh *SRNY M.S.* is about 2.8 times (7.08/2.55) that of the fresh catalyst, and the coke content of aged *SRNY M.S.* is about 3.0 times (2.67/0.89) that of the catalyst under the same pretreatment condition.

Effect of coking on surface pore structure of sample

The results of measurement of the specific surface area (*SSA*) and pore volume (*PV*) (or porosity) of the sample before and after coking are listed in Table 3.

The numerical changes in *SSA* and *PV* for fresh and aged samples reveal that the total specific surface area (*TSSA*), the micropore *SSA* and the total pore volume (*TPV*) of the coked fresh sample are less than those of the non-coked one. For example, the *TSSA* of fresh *SRNY M.S.* decreases from 520 to 288 $m^2 \cdot g^{-1}$ and the *TPV* from 0.310 to 0.199 $ml \cdot g^{-1}$, the percentage decreases being 44.6 and 35.8%, respectively. For the aged sample, the trend is the same, the *TSSA* of the coked and aged *SRNY M.S.* falling from 470 to 400 $m^2 \cdot g^{-1}$ and the *TPV* from 0.280 to 0.260 $ml \cdot g^{-1}$, but the percentage decreases are only 15.6 and 6.4%. For the catalyst, the effects of coking on *TSSA* and *TPV* are smaller than those on the *SRNY M.S.*; the percentage decreases in *TSSA* and *TPV* for the fresh sample being 30.0 and 17.0%, and for the aged sample 10.0 and 4.4%, respectively.

Table 3 Specific surface area and pore volume data before and after coking

Sample	Sample behaviour		Specific surface area / $m^2 \cdot g^{-1}$ total surface area	micropore surface area	outer surface area	Pore volume / $ml \cdot g^{-1}$ micropore volume	total pore volume
SRNY M.S.	fresh	non-coked	520	480	34	0.230	0.310
		coked	288	274	14	0.128	0.199
	aged	non-coked	474	440	34	0.200	0.280
		coked	400	383	17	0.176	0.260
SRNY catalyst	fresh	non-coked	303	140	163	0.070	0.300
		coked	212	72	140	0.035	0.249
	aged	non-coked	231	135	96	0.060	0.270
		coked	208	118	90	0.055	0.258
Support	fresh	non-coked	239	–	–	–	0.260
		coked	195	–	–	–	0.256
	aged	non-coked	231	–	–	–	0.284
		coked	121	–	–	–	0.271

From Table 3, it can readily be seen that the effects of coking on the *TSSA* and *TPV* of the support are much less obvious than those on the *SRNY M.S.*

When the data in Table 3 are further analysed, it is found that, regardless of whether they are fresh or aged, for the micropore structure of *SRNY M.S.* or the catalyst, the percentage decreases in their *MPV* are much higher than those for each *TPV*, but for the catalyst the phenomenon as stated above is much more obvious. Thus, it is reasonable to deduce that coke forms first in micropores of *SRNY M.S.*

According to the theory of Petersen, coking or fouling is a complex process involving precursor species formed from reactant and product species in the reaction mixture. However, from our experimental results, it may also be deduced that multiple layers of coke can indeed be adsorbed on the pore walls of the molecular sieve itself or the molecular sieve component in the catalyst, or even block its pores. It becomes clear that coke formation is directly related to the nature of the samples, which can be attributed to the acidity of the cracking catalyst, i.e. to the active sites on samples.

Relationship between coke content and acid amount of sample

In order to examine the relationship between the coke content and the acid amount of the sample, coke combustion experiments were carried out in an oxygen flow in different temperature ranges to obtain the coke content of the sample. According to Ref. [5], the acid amount can be measured through a series of corresponding temperatures after the coke has been burnt off. Data on the coke contents and the acid amount of samples measured at different temperatures are listed in Table 4.

Table 4 Data on coke contents and acid amount of samples

Pretreatment temperature/ °C	Sample behavior	*SRNY M.S.* coke amount mass/%	*SRNY M.S.* acid amount / $\mathrm{mmol \cdot g^{-1}}$	Catalyst acid amount / $\mathrm{mmol \cdot g^{-1}}$	Support acid amount / $\mathrm{mmol \cdot g^{-1}}$
500	fresh	0	1.482	0.800	0.589
620	fresh	0	1.278	–	–
340	coked	7.08	0.532	0.480	0.172
420	coked	6.36	0.649	0.533	0.279
520	coked	1.11	1.059	0.622	0.330
620	after coke burning	0	1.135	0.665	0.350

From the data listed in Table 4, the acid amount of *SRNY M.S.* apparently exhibited considerable differences because of the changes in coke content at the different pretreatment temperatures. The acid amount of fresh *SRNY M.S.* subjected to pretreatment at 500°C is 1.482 mmol·g^{-1}. This is much higher than that of the same kind of sample at 620°C: 1.278 mmol·g^{-1}.

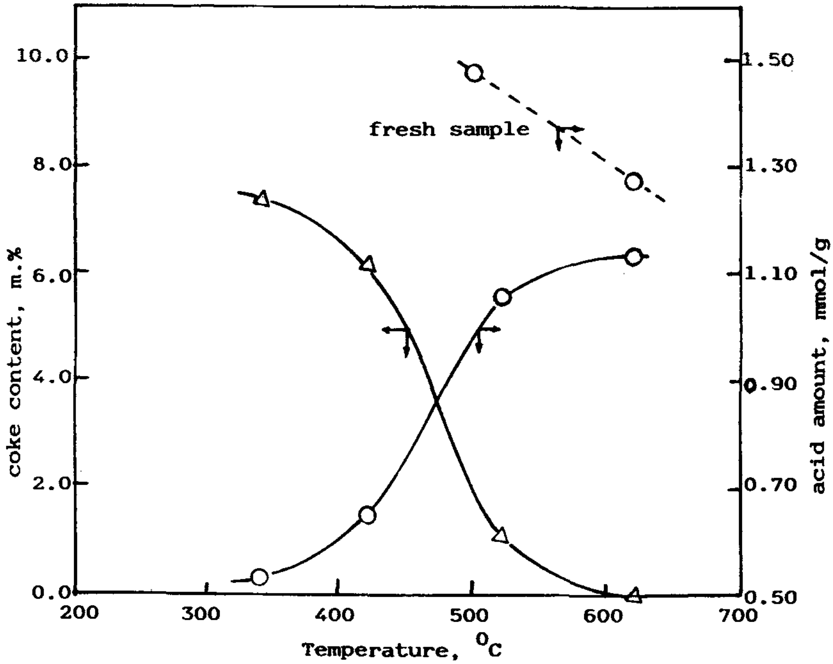

Fig. 1 Relationship between coke content, acid amount and temperature of burning off coke for *SRNY* molecular sieve

Using the data relating to *SRNY M.S.* in Table 4, the relationship between coke content and acid amount was plotted against the pretreatment or burning coke temperature (Fig. 1).

This difference in acidity found for the same kind of sample is possibly caused by the partial loss of hydroxy groups from *SRNY M.S.*, shown as a dotted line in Fig. 1. The higher the pretreatment temperature used, the more the hydroxy lost from the sample, and the less the acid amount remaining.

For the coked sample, the acid amount is restored through the decrease in the coke content due to the oxidation of carbonaceous deposits on *SRNY M.S.*, but even if the coke on the sample is completely burnt off, the acid amount can not be restored to the original level at 620°C. This can be attributed to irreversible polluting substances in the feedstock, which remain on some acid sites of the samples when these (such as *SRNY M.S.*) have reacted with *LDO*. From Fig. 1, it can be clearly seen that the acid amount increases with decrease of the coke content of the samples in a corresponding relationship. The catalyst or support exhibits a similar trend of change in acidity correlating with the pretreatment temperature.

Moreover, comparison of the acid strengths of fresh and aged *SRNY M.S.* before and after coking demonstrates that for fresh *SRNY M.S.* the stronger acid amount is 74.4% and that of the weaker is 25.6%, but after coking the stronger acid amount decreases to 67.0% and that of the weaker on increases to 33.0%. For aged *SRNY M.S.*, the stronger acid amount of the non-coked sample is 45.0% and that of the weaker one is 55.0%, but in the coked sample the stronger acid amount decreases to 29.0% and that of the weaker one increases to 71.0%.

It can be clearly demonstrated that the effect of coking on *SRNY M.S.* is most serious, and coke formation occurs mainly on the stronger acid sites on the samples.

Determination of kinetic parameter of coke combustion

An early study on the determination of kinetic parameters of a gas-solid reaction with *PTM*, using the DTA curve, was carried out by Kissinger in 1957 [6]. Later, the applicability of *PTM* to acquire kinetic parameters by means of thermal analysis was reexamined. Louis and Garcia-Cordorilla [7], who considered that Kissinger's *PTM* would apply completely to the DSC curve, examined an aluminium ally (AA1145) in a DSC experiment. Ingier-Stocka [8] demonstrated that Kissinger's formula is suitable to acquire kinetic parameters in the decomposition of $[Co(NH_3)_6]_2(C_2O_4)\cdot 4H_2O$ by means of DTA, TG and DSC, satisfactory experimental results being obtained.

Table 5 DSC data on kinetic parameter of coke combustion on sample

Sample	Condition	Peak temperature T_P/K*			Activation energy E / kJ·mol^{-1}	Preexponential factor A / min^{-1}	Average enthalpyΔH / J·g^{-1}
		a	b	c			
SRNY	fresh	753	775	797	125.1	1.37×10^{10}	554.2
M.S.	aged	766	791	811	123.6	7.25×10^{9}	210.4
SRNY	fresh	753	773	795	151.6	1.29×10^{12}	264.1
Catalyst	aged	761	782	802	157.6	2.60×10^{12}	77.9
Support	peak I	688	702	711	282.7	1.85×10^{23}	89.5
	peak II	737	761	787	120.6	1.12×10^{10}	
	peak III	818	828	839	364.3	1.45×10^{25}	

**a*, *b* and *c* represent the peak temperature at heating rates of 5, 10 and 20 deg min^{-1}, respectively

The present work, according to Kissinger's *PTM*, proves data relating to the kinetic parameters of coke combustion on a coked sample via DSC at different heating rates. The results are illustrated in Table 5.

It is clear from an analysis of the data in Table 5 that the activation energy of burning coke of *SRNY M.S.* is smaller than that for the catalyst, though the coke content of the former is greater than that of the latter, i.e. coke burns more easily on *SRNY M.S.* than on the catalyst. On the support, it is more complicated, and the real cause is not known. However, there is a definite correlating relationship between the average combustion enthalpy of the samples and their coke content .

Conclusions

1. TG and DSC are suitable procedures for the measurement of coke content, acid amount and/or kinetic parameters relating to coke combustion on solid catalyst samples.

From data obtained in thermal analysis experiments, one can characterize some properties of the given samples, and useful reference information on catalyst deactivation is obtained.

2. The results of experimental determinations in the present work show that in the *SRNY* catalyst system *SRNY M.S.* is the essential supplier of catalytic activity and is also the main site of coke formation. However, the activation energy data revealed that the coke on *SRNY M.S.* was burnt off more easily.

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Zusammenfassung — Aus einem handelsüblichen *SRNY* Molekularsieb (M.S.) wurde ein mit *SRNY* benannter Krack-Katalysator hergestellt. Das Trägermaterial besteht aus Kaolin, Ton und SiO_2. Mit leichtem Dieselöl (*LDO*) als Eintrag in einem Mikroreaktor wurde das Verkokungsverhalten des *SRNY M.S.*, des Trägermateriales und des Katalysators untersucht. Mittels Porenstrukturbestimmung und Thermoanalyse wurden die physikalisch-chemischen Eigenschaften von frischen und gealterten Proben in und außer der Krackreaktion von *LDO* charakterisiert. Die Porenstruktur umfaßt die spezifische Oberfläche und das Porenvolumen der Porösität. Thermoanalyse bedeutete in diesem Falle TG und DSC.

Die Ergebnisse zeigten, daß alle verkokten Proben im Vergleich zu nicht verkokten Proben eindeutige Änderungen der Oberflächenporenstruktur und Azidität aufwiesen. Spezifische Oberfläche und Säuregehalt sinken mit steigendem Koksgehalt in den Proben. Die scheinbare Aktivierungsenergie, die unter Einsatz einer temperaturprogrammierten Oxidationsmethode (*TPO*) an Entkohlungsproben in einem Luftstrom erhalten wurde, zeigte, daß sich die kinetischen Parameter des *SRNY M.S.* von denen des *SRNY*-Katalysators und des Trägermateriales unterscheiden.