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Influence of adsorption parameters on catalytic cracking and catalyst decay

A. Corma [a,*], F.J. Ortega [a,b]

[a] Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avda. de los Naranjos s/n, 46022 Valencia, Spain
[b] Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México DF, Mexico

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Abstract

Adsorption constants and heats of adsorption of different types of hydrocarbons on zeolitic catalysts have been obtained under cracking reaction conditions, by means of kinetic techniques. The heat of adsorption of a naphthene is very close to the alkane with the same number of carbon–carbon bonds, which in turn is defined by the van der Waals interactions between the hydrocarbon and the zeolite walls. The presence of the double bond in the olefin increases the heat of adsorption of the corresponding alkane by ∼40 kJ/mol. Comparison of decalin and tetralin shows the contribution of the aromatic ring to the heat of adsorption. Differences in heat of adsorption not only explain differences in cracking conversion, but can also predict variations in catalyst decay when industrial feeds of different compositions are used.

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1. Introduction

It is well known that adsorption of reactants on the catalyst surface is the first chemical step in a catalytic reaction. Adsorption is responsible for the preactivation of reactants, which results in a decrease of the activation energy of the process. It has been said, however, that in the case of catalytic cracking of alkanes with zeolites, the adsorption of the reactant corresponds to a van der Waals interaction between the alkane and the catalyst surface, and consequently the heat of adsorption is directly proportional to the number of carbons in the chain [1–4]. Then the apparent activation energy decreases when the number of carbon atoms in the reactant increases, but the true activation energy remains unchanged [5–8]. Babitz et al. found that when they cracked *n*-hexane over different zeolites (Y, mordenite, and ZSM-5), the apparent differences in activation energies are due to the different adsorption heats. Following these ideas, one could expect that the heat of adsorption of a long-chain olefin will have two components: one derived from the van der Waals interaction of the saturated part of the chain with the catalyst surface, and another, more localized, that may involve some electron transfer between the double bond and a Brønsted site of the catalyst. If this is so, a higher heat of adsorption for olefins than for paraffins would be expected. Likewise, hydrocarbon molecules containing aromatic groups should also have adsorption parameters different from those of either paraffins or olefins.

All this, which has its own interest from a fundamental point of view, for the rationalization of the adsorption interactions between solid catalyst and gaseous reactants, can also have important implications for the reaction of complex mixtures of molecules, since it occurs during catalytic cracking of industrial feeds. Indeed, in this case the feed or the partially cracked feed contains alkanes, alkenes, cycloalkanes, and aromatics. Thus, if one wishes to discuss feed reactivity, product selectivity, reaction kinetics, and catalyst decay, one should consider not only the differences in

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[*] Corresponding author. Fax: +34 96 3877809.
E-mail address: acorma@itq.upv.es (A. Corma).

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the intrinsic cracking rate of the group of molecules mentioned above, but also the differences in adsorption.

For instance, in the case of catalytic cracking, because of the lack of data, most authors make use of kinetic models that do not include adsorption parameters. However, adsorption and desorption parameters can play an important role in some cases [9]. Pruski et al. and Gianetto et al. have determined adsorption coefficients for gasoil and its lumped reaction products, showing the relevance of adsorption phenomena for catalytic cracking [10,11]. The same observations were made by Zhao and Wojciechowski when they cracked 2-methylpentane [12]; they also showed the impact of the heat of adsorption of reactants and products on catalyst decay. Bokhoven et al. used the Langmuir–Hinselwood formalism to show the dominant role of reactant sorption under conditions in which catalyst deactivation is considered negligible [13].

Although it is true that it is possible to carry out in situ adsorption measurements by means of techniques such as infrared spectroscopy, nuclear magnetic resonance, or calorimetric methods, among others, it is also true that such measurements are usually performed under conditions far from those under which the catalytic reactions occur.

Kinetic studies using pure compounds, on the other hand, can be used to determine adsorption parameters under reaction conditions. Kinetic equations may also provide valuable information on product adsorption and its effect on catalyst deactivation.

In the present work, we report results for cracking of some pure hydrocarbons (an alkane, an alkene, a cycloalkane, and an aromatic) over a commercial FCC catalyst containing USY zeolite. The corresponding kinetic and adsorption parameters of reactants and products were determined.

2. Experimental

2.1. Materials

1-Octene (Fluka; 99%), *cis–trans* decalin (Aldrich; >97%), and tetralin (Aldrich; >99%) were used as feedstocks without any further treatment.

A commercial low rare earth USY FCC catalyst (whose properties are listed in Table 1) was used to carry out the experimental work. Before the catalytic experiments, fresh catalyst was equilibrated by a steam treatment at 1089 K for 4 h with a mixture of 90 wt% steam and 10 wt% air. With this treatment the unit cell size of the zeolite in the catalyst was stabilized to 2.425 nm.

2.2. Experimental procedure

Experiments were performed in an automated computer-controlled micro activity test unit (MAT), which can carry out up to eight continuous experiments. Details of the apparatus and methodology have been described previously [14]. Each experiment consisted of a four-step cycle: stabilization, reaction, stripping, and regeneration. During the 30 min of the stabilization step, nitrogen is injected at a rate of 50 cc/min through the reactor, allowing temperatures to stabilize at the preset reaction temperature value. Before reaction, feed is pumped for 15 s into a purge collector to prevent any gas bubbles from entering the reactor. Then the feed is injected through the fixed-bed reactor and the reaction products are recovered in a cooled sampler. Liquid products are condensed in the sampler, and gases flow into an atmospheric burette, where they are accumulated for further analysis. After the reaction step, 100 cc/min of stripping nitrogen is fed through the catalytic bed for 15 min. Nitrogen sweeps liquid and gaseous hydrocarbons from the catalytic bed, and products are recovered in the cooled sampler and in the gas burette. To regenerate the deactivated catalyst, the coke produced by the reaction and deposited on the catalyst surface is burned off. Air is fed at a rate of 100 cc/min, and the flue gas from the reactor is sent into a catalytic furnace packed with copper oxides, where carbon monoxide is converted into carbon dioxide. After regeneration the catalyst is ready to start a new cycle.

Table 1
Catalyst properties

	Method	Fresh	Equilibrated
Bulk density (g/cc)	UOP-254	0.9	0.905
Specific area (m^2/g)	ASTM-D-3663	412	277
Zeolite specific area (m^2/g)	ASTM-D-3663	272	170
External specific area (m^2/g)	ASTM-D-3663	139	107
Pore volume (cc/g)	ASTM-D-4222	0.198	0.218
Unit cell size (Å)	ASTM 3942/80	24.49	24.25
Average particule size (μm)	ASTM-D-4464	70	70
Silica/alumina	–	6	60
Rare earths oxides (wt%)	IMP-QA-803	1	1

Thus, 3.0 g of equilibrated catalyst was loaded into the catalytic bed, and, after each set of experiments, the catalyst was discharged and characterized for a specific surface area and zeolite unit cell size. A bed of 3 cm of silicon carbide was placed above the catalyst bed as a preheater to ensure feed vaporization. A blank test was run for each hydrocarbon to measure thermal cracking, which resulted in less than 1.0 wt% at 773 K.

Conversion versus time on stream curves was built up in the range of 5–120 s while the feed flow and catalyst mass were kept constant. By doing this it was possible to observe the catalyst decay. To obtain data at different contact times, experiments were performed at different feed flows, 3.0, 4.0, and 5.0 g/min, respectively, over a catalyst mass of 3.0 g. Likewise, we monitored thermal effects by performing the experiments at two reaction temperatures, 673 and 773 K.

Catalyst stripping was done at reaction temperature with a flow of nitrogen at 100 ml/min, and catalyst regeneration was carried out at 813 K.

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