THE EFFECT OF COMPOSITION OF COBALT-MOLYBDENUM CATALYSTS ON THEIR SURFACE ACIDITY AND ISOMERISATION ACTIVITY

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Kinetics of isomerisation of cyclohexene to methylcyclopentene proceeding as parallel reaction to hydrogenation of cyclohexene to cyclohexane on cobalt-molybdenum catalysts of different composition has been measured. The surface acidity of these catalysts was estimated from the difference in the adsorption of toluene and heptane which was measured by chromatographic method. In a series of catalysts containing molybdenum the acidity parallels isomerisation activity. Cobalt on alumina catalysts and alumina itself have greater acidity but exhibit lower isomerisation activity compared to the catalysts containing molybdenum.

A mixed Co–Mo–Al_2O_3 sulphided catalyst has polyfunctional character[1]. It catalyses hydrogenation-dehydrogenation reactions but also reactions in which the acidity of the catalyst plays a role, such as isomerisations of saturated and unsaturated hydrocarbons, hydrogen sulphide elimination from sulphides *etc.* Even sulphides themselves have polyfunctional character[2–4] and alumina used as their carrier stresses this feature. Hydrogenation-dehydrogenation and acidic properties are complementary in some reactions, *e.g.* in isomerisation of saturated hydrocarbons[1,3]. Also hydrodesulphuration of thiophene on these catalysts can be explained as a two-step reaction involving in the first step hydrogenation of thiophene to tetrahydrothiophene, in which hydrogenation activity of the catalyst plays a role, and elimination of hydrogen sulphide from tetrahydrothiophene without participation of hydrogen in the second step, in which acidic properties of the catalyst play a decisive role[5].

In the present work we made an attempt to ascertain how the surface acidity and activity of Co–Mo–Al_2O_3 catalysts in isomerisation of cyclohexene to methylcyclopentene changes with their composition. Surface acidity was characterized by the difference between toluene and n-heptane adsorption determined chromatographically. This method was used earlier to follow the acidity of Al_2O_3–SiO_2 and Al_2O_3–MgO (ref.[6]), MoS_2 and Al_2O_3 catalysts and of one sample of industrial Co–Mo–Al_2O_3 catalyst[7]. Isomerisation of cyclohexene was followed by the method of initial reaction rates using a flow reactor and atmospheric pressure. Data on parallel hydrogenation of cyclohexene to cyclohexane and also on hydrodesulphuration of thiophene are reported elsewhere[8].

EXPERIMENTAL

Catalysts used in this work were prepared by impregnation of industrial alumina by ammonium paramolybdate and cobalt(II) nitrate. The preparation of catalysts and the procedure used for their activation prior to measurements in the reactor are described elsewhere[8]. Their designation, composition and BET surface are given in Table I.

Kinetic data were obtained in a flow pseudo-differential reactor by the method of initial reaction rates. Experimental procedure used in measurements is reported in detail elsewhere[8]. Reaction rates r_I^0 were determined from dependences of the conversion of cyclohexene to methylcyclopentene x_I on the reciprocal value of space velocity W/F_C which were linear in the conversion region used (x_I 0—3%). Parallel reaction to isomerisation was hydrogenation of cyclohexene to cyclohexane.

Adsorption was measured with the use of the same apparatus and by the same way as in the previous work[7]. The sulphided catalyst[8] (6—8 g) was heated successively in a stream of He, H_2 and again He, each for one hour prior to measurement. For comparison of adsorption on different catalysts we used the ratio $c_{0.1} = s/p$ where s is the adsorbed amount at an adsorbate pressure of 0·1 kPa and p is the adsorbate pressure (0·1 kPa). This ratio was considered as approximation of adsorption capacity in the origin of adsorption isotherm[7]. The adsorbed amount s at pressure p was determined as the integral $(1/RTm) \int_0^p V \, dp$ where the dependence $V = f(p)$ is determined by asymmetric peak tail[9].

RESULTS AND DISCUSSION

Isomerisation of cyclohexene was followed at 350°C and partial pressure of cyclohexene $p_C = 0{\cdot}008$ to 0·1 MPa and of hydrogen $p_H^0 = 0$ to 0·092 MPa. Under these conditions and on all the catalysts containing molybdenum isomerisation of cyclohexene to methylcyclopentene is accompanied by parallel hydrogenation of cyclohexene to cyclohexane, the kinetics of which was reported in a previous communication[8]. The rate of hydrogenation, and therefore the ratio of rates of both reactions, depends on the partial pressure of hydrogen. Isomerisation prevails at the ratios N_C^0 greater than c. 0·5, while hydrogenation[8] is the main reaction at N_C^0 smaller than 0·5, in accordance with the results of other authors obtained for an industrial Co–Mo–Al_2O_3 catalyst[10]. At the higher hydrogen pressure than atmospheric, the rate of hydrogenation further increases and isomerisation becomes relatively unimportant[4]. Hydrogenation of methylcyclopentene to methylcyclopentane proceeds[10] consecutively to isomerisation of cyclohexene to methylcyclopentene. In our measurements of initial reaction rates, in which cyclohexene conversions to methylcyclopentene were lower than 3%, methylcyclopentane was not present among reaction products in significant amounts. On Co–Al_2O_3 catalysts and on Al_2O_3 itself hydrogenation of cyclohexene to cyclohexane did not take place under conditions used.

Dependences of initial reaction rates of isomerisation on N_C^0 ratio are represented graphically in Fig. 1. The kinetic curve for $p_C^0 + p_H^0 = 0{\cdot}08$ MPa lies between data for $p_C^0 + p_H^0 = 0{\cdot}1$ MPa and 0·06 MPa and for the sake of clarity it is not shown in the figure. Kinetic data $r_I^0 - p_C^0 - p_H^0$ were correlated by several Langmuir–Hinshelwood equations and by power type equations, using the method of nonlinear regression[8] and Eq. (*1*) was selected as that describing best experimental data. Obtained kinetic constants and adsorption coefficients (Eq. (*1*)) are given in Table I. The curves fitted to experimental points in Fig. 1 are calculated according to Eq. (*1*) with the use of the constants from Table I.

$$r_I^0 = k_I K_I p_C^0 / (1 + K_I p_C^0) \qquad (1)$$

Obtained $c_{0.1}$ ratios, characterizing the extent of adsorption, are presented in Table I. Aromatic hydrocarbons are weak Lewis bases (π-bases) and form complexes with a variety of electron acceptors, *e.g.* with proton, metal cations, π-acids such as tetracyanoethylene or trinitrotoluene *etc.*[11,12]. Saturated hydrocarbons are inert toward acids and the fact that aromatic hydrocarbons adsorb more strongly on the surface can be ascribed to specific interaction of π-electrons of benzene with acidic sites of the surface. The measure of acidity is then the difference

$$a = \log\left(c_{0.1}\,(\text{toluene})\right) - \log\left(c_{0.1}\,(\text{heptane})\right), \qquad (2)$$

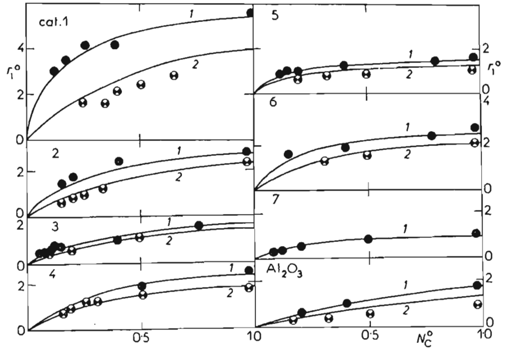

FIG. 1

Dependence of r_I^0 on the Composition of Feed for Different Catalysts

Points are experimental data, curves are calculated according to Eq. (*1*). *1* $p_C^0 + p_H^0 = 0{\cdot}1$ MPa, *2* $p_C^0 + p_H^0 = 0{\cdot}06$ MPa.

TABLE I

Designation, Composition and Measured Properties of Catalysts

Catalyst		$\frac{Co+Mo^a}{Al_2O_3}$	$\frac{Co^a}{Mo}$	Surface BET^b	k_I	K_I	k_IK_I	c_0(toluene)	c_0(heptane)	^{a}
Co–Mo–Al_2O_3	1	0·15	0·2	215	6·3	64	403	6·0	3·0	0·30
	2	0·05	0·2	219	3·4	38	130	7·1	4·5	0·20
	3	0·10	0·2	205	1·6	52	83	9·3	5·5	0·23
	4	0·10	0·5	230	3·0	33	99	8·5	5·0	0·23
	5	0·10	1·0	218	1·7	68	116	5·6	3·4	0·22
Mo–Al_2O_3	(6)	0·10	0	188	2·9	53	154	8·0	5·3	0·18
Co–Al_2O_3	(7)	0·10	—	—	1·4	31	43	13·8	4·6	0·48
Al_2O_3		0	—	230	3·3	11	36	9·1	3·8	0·38

^{a} mol/mol, ^{b} $m^2 g^{-1}$.

which is proportional to the contribution of this specific interaction to ΔG of adsorption (ref.[13]) The acidity estimated by this way cannot be discussed in terms of the classification of acidic sites as Lewis or Bronstedt sites since the basicity of aromatic hydrocarbons is of such type that they interact with both. As it is seen from Table I, all the catalysts containing both cobalt and molybdenum have smaller acidity than alumina itself, which agrees with our earlier observations[7,14]. Clearly the most acidic among these catalysts is Co–Mo–Al_2O_3, sample 1, which exhibits also the greatest isomerisation activity expressed by the product of the rate and adsorption constant, presented in Table I. The greatest isomerisation activity of this catalyst is obvious qualitatively also from Fig. 1. Co–Mo–Al_2O_3 catalysts Nos 2 to 4 show smaller and mutually comparable acidity and isomerisation activity. This rough correlation between acidity and activity holds also for the Mo–Al_2O_3 catalyst which shows a similar acidity and isomerisation activity as Co–Mo–Al_2O_3 catalysts 2 to 4. This trend is not valid for the catalysts without molybdenum, *i.e.* for Co–Al_2O_3 catalyst and alumina itself, which exhibit high acidity but low isomerisation activity. This demonstrates that the catalysts containing molybdenum differ from Co–Al_2O_3 and Al_2O_3 catalysts either by the character of acidity, *i.e.* the quality and distribution of acid sites, or by the mechanism of isomerisation, eventually by both factors. Different character of their acidity is very probable. The addition of MoO_3 to Al_2O_3 changes the character of acidity of alumina and the addition of cobalt affects the acidities of MoO_3–Al_2O_3 and Al_2O_3 in different ways[15]. Furthermore, the samples in this work were sulphided, which further extends the choice of possible acid sites. These may be protons of SH or OH groups, cations of present metals. Also the role of nonstoichiometric sulphur could be taken into account. Another reason why the catalysts not containing molybdenum do not follow the above mentioned parallelity of the acidity and isomerisation activity observed for molybdenum catalysts may be the change in isomerisation mechanism Isomerisation of olefins does not seem to be exclusively acid catalysed reaction; it takes place also on the catalysts which do not exhibit acidic properties, *e.g.* on pure platinum[16]. In such a case, the acidity becomes only one of the factors determining isomerisation activity. As a result a more general correlation of acidity with isomerisation activity cannot be expected to exist when a more significant change in chemical composition of the catalyst is taking place, such as is the substitution of catalyst containing molybdenum for the catalyst without this metal.

Data on isomerisation in Table I and data on hydrogenation reported in a previous work[8] show that the activity for isomerisation and hydrogenation do not change parallel to the catalyst composition. Provided that hydrodesulphuration of thiophene is bifunctionally catalysed reaction[5] involving hydrogenation of thiophene to tetrahydrothiophene followed by decomposition of tetrahydrothiophene without participation of hydrogen, one can expect a complex dependence of hydrodesulphuration activity on the composition of catalyst, as found in a previous work[8]. This dependence can be furthermore strongly influenced by hydrogen pressure, since both reactions show different pressure dependence.

LIST OF SYMBOLS

a	relative acidity
c_0	adsorption capacity (ds/dp) in the origin of isotherms [μmol g^{-1} kPa^{-1}]
$c_{0.1}$	adsorption capacity at 0·1 kPa pressure [μmol g^{-1} kPa^{-1}]
F	feed rate [mol h^{-1}]
k_I	rate constant for cyclohexene isomerisation [mol h^{-1} kg^{-1}]
K_I	adsorption coefficient of cyclohexene in isomerisation [MPa^{-1}]
m	mass
N_C^0	initial mole fraction
p	pressure of adsorbate [kPa]
p^0	initial partial pressure [MPa]
r_I^0	initial reaction rate of isomerisation of cyclohexene [mol kg^{-1} h^{-1}]
s	adsorbed amount [μmol g^{-1}]
R	gas constant
T	temperature
V	volume
W	catalyst weight [kg]
x_I	conversion of cyclohexene to methylcyclopentene

Indices

H	hydrogen
C	cyclohexene
I	isomerisation

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