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A NEW METHOD FOR POISONING SURFACE ACTIVE SITES: ADSORPTION OF HAMMETT INDICATORS

By

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Abstract

The new method of poisoning acid and base surface sites is demonstrated. The proposed method is based on adsorption of stoichiometric amounts of Hammett indicators in relation to surface base or acid centres of established strength. The poisoning with usage of Hammett indicators was tested in reactions of alkenes isomerization over superbase catalysts, decomposition of diacetone alcohol over NaOH doped magnesia and transformation of methanol over MgO. Suppressing the basic sites with Hammett indicators was also exploited as a means to prove the coexistence of superbase and one-electron donor sites on magnesia.

Introduction

Recently, Hammett indicators have found a wide application in the examination of acid-base properties of heterogeneous catalysts. Visual or spectrophotometric observation of the colour change of an adsorbed indicator makes possible the assessment of the basic or acid strength of the surface. Hammett indicators are also indispensable in quantitative measurements of acidity or basicity of the surface by methods advanced by Benesi,^{1,2)} Yamanaka and Tanabe^{3,4)} and Take *et al.*⁵⁾

The acid strength of the surface is defined as its ability to convert an adsorbed neutral base into its conjugate acid form and is expressed by the Hammett acidity function:

$$H_0 = pK_{BH^+} + \log \frac{[B]}{[BH^+]}$$

The basic strength is defined as the ability of the surface sites to convert

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an adsorbed electrically neutral acid into its conjugate basic form and is given by the Hammett basicity function :

$$H_- = pK_A + \log \frac{[A^-]}{[AH]}.$$

In measurements of acidity or basicity of the surface the Hammett indicators play the role of either base or acid. Assuming that the observed colour change of the adsorbed indicators corresponds to the conversion of 50% of neutral molecules into the conjugate acid or base, respectively, the acid strength of the surface can be represented as follows :

$$H_0 = pK_{BH^+} \quad \text{of indicator}$$

and similarly the basic strength :

$$H_- = pK_A \quad \text{of indicator.}$$

The indicator method permits fast and easy evaluation of surface acidity or basicity. Furthermore if a large variety of indicators is used of which one differs from another by about one pK_a or pK_{BH^+} unit it becomes possible to determine precisely the acid-base properties of a solid.

Extensive application of Hammett indicators for determination of acidity (titration with *n*-butylamine solution) or basicity (titration with benzoic acid solution) entailed investigation of the nature of their adsorption on heterogeneous surface. Thus it was concluded that the adsorption equilibrium sets in rapidly and binding forces are so strong that displacement of the adsorbed indicator by *n*-butylamine, a strong base, proceeds at exceedingly low rate.^{2,6)} In the case of basicity indicators such as diphenylamine or aniline the entire depletion of adsorbed molecules is never reached even in the presence of benzoic acid.⁷⁾ The properties of Hammett indicators, namely the selectivity of interaction with adequate active sites, the irreversibility of this interaction and its high velocity made these compounds useful in the investigation of heterogeneous catalysts. Taking into account all the above merits of Hammett indicators we have made an attempt to use them as poisons of active sites involved in catalytic reactions. So far, only a limited number of acids or bases have been used as poisons of active surface sites, *e.g.*, ammonia, pyridine or *n*-butylamine have been described as poisons of acid type sites whereas phenol has usually been referred to as a poison of basic sites. However, with these substances it is impossible to determine the range of strengths of active sites being poisoned. Another disadvantage is that some of the above substances may exhibit both basic and acid properties and react with acid as well as basic sites, *e.g.*, ammonia is known to react with Al_2O_3

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surface to give simultaneously NH_4^+ and NH_2^- surface species. Moreover, the desorption of "traditional" poisons is greatly enhanced by temperature. On the other hand the Hammett indicators are adsorbed almost irreversibly. Once adsorbed they may be displaced only by strong acids or bases. Since most reagents of catalytic reactions display rather weak acid or base properties they are not expected to displace the adsorbed Hammett indicators. Usage of indicators with gradually increasing pK_a values as poisons of surface basic sites permits precise determination of the strengths of the sites responsible for the catalyst activity in a given reaction. Indicators characterized by the highest pK_a values (the weakest acids) react exclusively with the strongest basic sites, while those with lower pK_a 's cover a greater range of basic strengths. Hence, a substantial change in the composition of reaction products or its velocity due to modification of the surface with an indicator of a particular pK_{ai} indicates that sites whose $\text{H}_- \geq \text{pK}_{ai}$ are involved in a catalytic reaction. To obtain the most reliable and precise results it is essential that the indicator be used in a stoichiometric quantity with respect to surface sites of the corresponding strength. If the amount of an indicator exceeds that of the corresponding active sites, the remaining active sites may be also blocked by physically adsorbed molecules of an indicator.

The poisoning method was used by us in the investigation of a set magnesia-supported basic catalysts. Hammett indicators were used as poisons towards :

1. isomerization of alkene over superbase catalysts MgO-metallic sodium
2. decomposition of diacetone alcohol over NaOH-doped magnesia
3. transformation of methanol over magnesia.

Suppressing the basic sites with Hammett indicators was also exploited as a means to prove the coexistence of base and one-electron donor sites on magnesia.

Experimental

Adsorption of Hammett indicator was carried out at room temperature from water and oxygen free benzene solutions. When employed for studies of alkenes isomerization and decomposition of diacetons alcohol the solutions contained stoichiometric amounts of indicators with respect to the number of the corresponding active sites. Magnesium oxide used as catalyst in methanol conversion was poisoned with 5% benzene solutions of indicators. The procedure of an indicator adsorption was as follows. The suspension of a freshly calcined catalyst in an appropriate solution was stirred for 3 hr. Subsequently the excess of liquid was removed and the catalyst was rinsed

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with oxygen and water free benzene to wash away the physically adsorbed indicator. The remaining benzene was then removed under vacuum (10^{-2} Torr). The whole operation was performed under dry, deoxidized nitrogen. An indicator-doped catalyst was then placed in a catalytic reactor. Isomerization of alkenes and decomposition of diacetone alcohol were carried out in a batch-type reactor at ambient temperature. The conversion of methanol was studied within $250\sim 450^{\circ}\text{C}$ using a fixed bed flow reactor.

High temperature of methanol conversion imposed the necessity of testing the thermal stability of indicators in the presence and absence of the catalyst. For this purpose the typical flow reactor with fixed catalyst bed was used. Five percent benzene solutions of various indicators were passed over quartz pieces or magnesia granules at temperatures from 250 to 450°C . In this way we examined the properties of the following indicators: aniline ($\text{pK}_a=27$), 4-chloroaniline ($\text{pK}_a=26.5$), 4-chloro-2-nitroaniline ($\text{pK}_a=18.2$) and *m*-dinitrobenzene. At temperatures equal to or lower than 350°C no conversion of either of the indicators was noted, whereas over 350°C , traces of decomposition products were detected. Thus it was concluded that side reactions of adsorbed indicators would not obscure results of the tested methanol conversion. It should be emphasized that products of methanol conversion were not contaminated with the indicator itself as its decomposition products at any reaction temperature.

Results

Isomerization of alkenes

It was previously observed⁸⁻¹⁰ that sputtering the magnesia surface with metallic sodium leads to the formation of superbases ($\text{H}_- \geq 35$) and extremely strong one-electron donor centres. Depending on the temperature of MgO pretreatment prior to sodium deposition either superbase (temperature of precalcination between 550 and 650°C) or one-electron donor (calcination temperature of 700 to 1000°C) properties will dominate.

Over catalysts with predominating superbase sites (Table 1) pentene-1 was found to isomerize to a mixture of 97% of pentene-2, the *cis/trans* ratio being *ca.* 0.3 and a remaining pentene-1. If however the catalysts displaying predominant one-electron donating properties were used the isomerization products contained 90% of pentene-2, the *cis/trans* ratio being *ca.* 3, and pentene-1.

Pure magnesium oxide was completely inactive in isomerization of alkenes under adopted conditions (room temperature, alkene in liquid phase). Since pure MgO showed any isomerizing activity it was reasonable to link the

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TABLE 1. The composition of the products of pentene-1 isomerization over MgO-Na_m catalysts

Catalyst	Calcination temperature of MgO (°C)	Initial reaction rate* (%/min)	Initial cis/trans ratio of pentene-2	cis/trans ratio of pentene-2 after 2 hr.	pentene-1 conversion after 2 hr. (%)
MgO-Na _m	550	5.9	1.80	0.29	98.5
MgO-Na _m	650	16.7	1.67	0.20	98.0
MgO-Na _m	700	3.9	2.43	1.02	95.5
MgO-Na _m	750	4.2	3.30	1.83	87.0
MgO-Na _m	1000	3.2	3.23	2.53	49.0
MgO-Na _m poisoned with triphenylmethane	550	3.5	3.30	3.20	38.2
MgO-Na _m poisoned with triphenylmethane	700	3.3	3.25	2.60	70.0

* Calculated from pentene-1 uptake.

observed activity with active sites existing only on the metallic sodium doped catalysts, *i. e.*, superbasic sites ($H_{-} \geq 35$) and very strong one-electron donor sites.

Taking into consideration the fact that for all catalysts studied the initial cis/trans ratio was greater than 1 (Table 1) it was inferred that the isomerization was a two-stage reaction involving a primary isomerization to produce a mixture of pentene-2 isomers with cis/trans > 1 and a consecutive isomerization of cis pentene-2 to trans isomer. The contribution of the second step becomes particularly significant if the superbase properties of the catalyst prevail. Hence, it seems likely that the two-electron donor sites are responsible for the second step of isomerization.

In order to verify this supposition triphenylmethane ($pK_a = 33$) was adsorbed on sodium doped magnesia precalcined at 650 and 700°C, respectively. Upon adsorption of triphenylmethane the catalysts were used in isomerization of pentene-1 (Table 1). After 2 hr. of reaction the cis/trans ratio of pentene-2 isomers changed in favour of cis pentene-2. Isomerizing activity of both catalyst poisoned with triphenylmethane was close to that of sodium-magnesia system (containing magnesia pretreated at 1000°C) which is known to possess no superbase sites. The decrease in the conversion of pentene-1 after 2 hr. of reaction is eventually due to shielding some of the one-electron donor sites by physically adsorbed poison.

To check the hypothesis that the two-electron donor (basic) sites are

responsible for the second step of the reaction, the isomerization of trans pentene-2 to cis pentene-2 was carried out over magnesium oxide calcined at 1000 and 650°C doped with metallic sodium. The two catalysts are the ones most distinctly varying in physicochemical properties (basic and one-electron donor). The catalyst obtained from MgO treated at 1000°C exhibited no activity towards the isomerization of trans pentene-2, whereas the reaction was observed to proceed over the second catalyst to yield after 2 hr. a mixture of cis (11.5%) and trans (87%) pentene-2 and pentene-1 (1.5%). Blocking the superbases centres of this catalyst with a stoichiometric quantity of triphenylmethane rendered the catalyst entirely inactive towards isomerization of trans pentene-2. These results confirm our suggestion about the alkene-1 isomerization pathway over series of catalysts under study.

The magnesia-sodium catalysts turned out to be remarkably active in isomerization of hexene-1, the products being cis and trans hexenes-2 and isomeric hexenes-3. Hexene-1 behaves similarly to pentene-1. Over catalysts with superbases sites the trans hexene-2 is the favoured product whereas over those with predominant one-electron donor sites the cis hexene-2 is the main product. Moreover, superbases catalysts considerably facilitate the formation of hexenes-3 as contrasted to one-electron donor ones. A similar experiment, involving adsorption with triphenylmethane, was run with hexene-1. The catalyst possessing the greatest quantity of superbases sites was chosen and the latter were blocked with triphenylmethane in the amount stoichiometrically equivalent to that of sites to be blocked (Table 2). Blocking

TABLE 2. The composition of the products of hexene-1 isomerization over MgO-Na_m catalysts

Catalyst	Calc. temp. of MgO (°C)	Initial cis/trans ratio of hexene-2	cis/trans ratio of hexene-2 after 2 hr.	hexenes-3 content after 2 hr.	hexene-1 conversion after 2 hr. (%)
MgO-Na _m	550	0.80	0.75	9.5	78
MgO-Na _m	650	0.70	0.60	15.2	89
MgO-Na _m	700	1.50	1.30	5.7	74
MgO-Na _m	750	1.60	1.55	4.2	72
MgO-Na _m	1000	2.20	1.80	1.8	44
MgO-Na _m poisoned with triphenylmethane	650	1.60	1.40	2.5	61.5
MgO-Na _m poisoned with nitrobenzene	650	0.65	0.50	2.6	5.2

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of superbase sites results in the increase of selectivity towards cis hexenes-2 and the decrease in the yield of hexenes-3. On the surface of the same catalyst the adsorption of nitrobenzene was performed. Nitrobenzene is poison both to the strongest one-electron donor and superbasic centres. In the presence of poisoned catalyst the almost complete decay of isomerization of hexene-1 was observed (Table 2). It may be explained by the fact that in this case all hypothetically active sites for isomerization reaction were blocked by the poison.

From the above experimental results it follows that isomerization of both pentene-1 and hexene-1 over catalysts studied is a two-steps process, the first step being the isomerization of alkene-1 to give a mixture of cis and trans alkenes-2, in which both one-electron donor and superbasic sites are active, and the second being the consecutive isomerization of cis alkene-2 into trans alkene-2, the latter proceeding exclusively on superbase sites. It is also supposed that further transformation of hexenes resulting in the formation of hexene-3 isomeric mixture is catalysed by superbase sites.

The additional evidence of the activity of one-electron donor sites in the first step of isomerization reaction was obtained via adsorption experiments. Adsorption of pentene-1 vapours at room temperature on the surface of investigated catalysts provide to the formation of paramagnetic species observed using ESR spectroscopy method. The changes of the intensity of the ESR signal derived from this species ($g=2.0012$) in the series of examined catalysts were conform with the changes of the strongest one-electron donor centres concentration. This in connection with poisoning results seems to prove the activity of strong one-electron donor sites in isomerization of alkenes in examined systems.

Decomposition of diacetone alcohol

Catalytic activity of bases in decomposition of diacetone alcohol has been first demonstrated by Koelichen.¹¹ He found that the reaction proceeds in the solutions of alkaline hydroxides through stages analogous to these of aldol condensation. Fukuda *et al.*¹² have shown that in the presence of alkali metal oxides the decomposition of diacetone alcohol is a first order reaction with respect to acetone and observed the correlation between the reaction rate and the concentration of basic sites at a strength of $H_- \geq 12.2$. Our studies concerned a series of catalysts obtained by doping MgO with various amounts of NaOH (from 0.005~0.82 mmole NaOH/g MgO).¹³ The conversion of diacetone alcohol proceeds over all catalysts with the formation of unidentified light brown substance which gradually covers the grains of the catalyst. A similar phenomenon was observed by Tada¹⁴ who investi-

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TABLE 3. Initial rates of reaction of decomposition of diacetone alcohol in the presence of series of MgO-NaOH catalysts

Sodium content in the catalyst mmol/g MgO	0	0.005	0.01	0.07	0.35	0.82	0.01 poisoned with 4-chloro-2-nitroaniline	0.01 poisoned with trinitroaniline	0.01 poisoned with aniline	0.01 poisoned with benzylacetophenone
Initial reaction rate %/min·m ²	0.10	0.15	0.16	0.16	0.39	0.25	0.13	0	0.155	0.13

gated the decomposition of diacetone alcohol over alkali metal phosphates. The unidentified substance is probably the product of consecutive condensation of acetone. To minimize the influence of consecutive reactions the initial rates of acetone formation were taken as a measure of catalytic activity. A correlation was found between the initial reaction rate and the concentration of basic sites at strengths of $12.2 < H_{-} \leq 15$. Several basicity indicators and an acidity indicator (benzylidenoacetophenone) were adsorbed on a randomly chosen catalyst (the one chosen had 0.01 mmole Na⁺/g MgO) and diacetone alcohol conversion was performed therewith. The results obtained confirmed our suppositions. Poisoning the sites at basic strengths of $12.2 < H_{-} \leq 15$ results in an entire disappearance of the activity towards diacetone alcohol decomposition. It is however astonishing that blocking the sites at greater strengths has no apparent effect on the reaction rate. It is not unlikely that adsorption of relatively acidic diacetone alcohol on this sites is strong and practically irreversible at room temperature or that it leads to other than acetone reaction products (unidentified brown residue). The slight decrease in the initial rate of reaction observed in the case of poisoning the stronger basic and acid sites can be explained by shielding effect of physically adsorbed indicator.

Thus, adsorption of Hammett indicators on the catalyst surface once again proved useful in ascribing the activity of a catalyst to particular type of sites on its surface.

Methanol conversion

In the presence of magnesia calcined at temperatures higher than 500°C under inert gas atmosphere, methanol decomposes to give hydrogen and carbon monoxide. The reaction products contain also some amount of formaldehyde. Therefore it is supposed that the reaction involves two steps:

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1. $\text{CH}_3\text{OH} \longrightarrow \text{CH}_2\text{O} + \text{H}_2$
2. $\text{CH}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$

Since the magnesium oxide is one of the strongest solid bases, and its acid properties are insignificant it can be expected that methanol conversion involves exclusively basic sites of the catalyst. Assuming the validity of generally accepted mechanism of transformations over basic catalysts one can surmise the following pathway for methanol conversion :

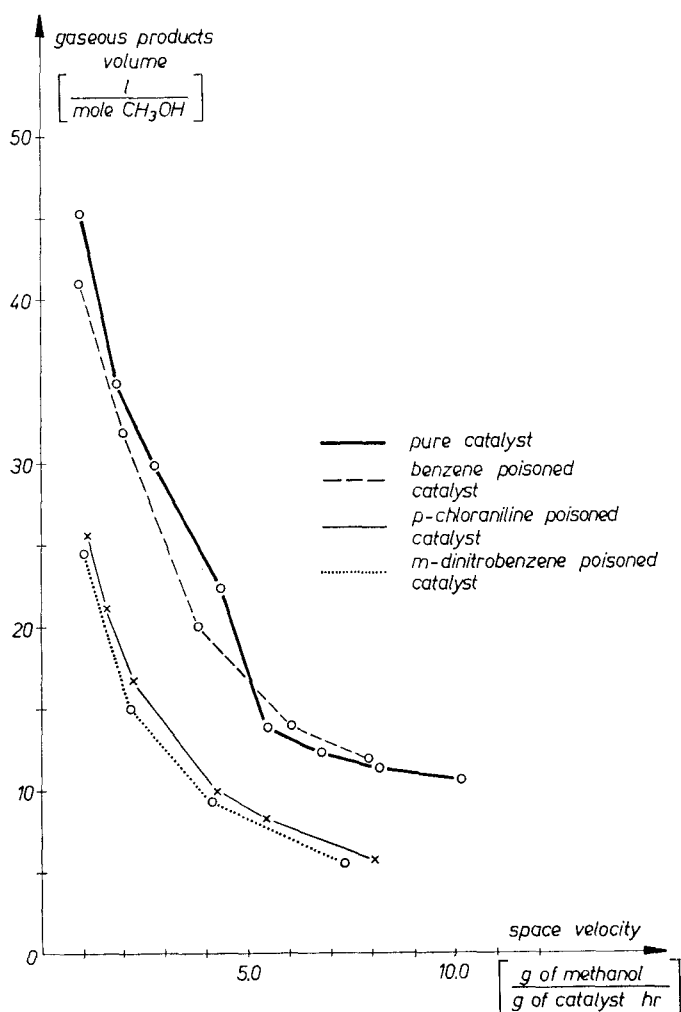
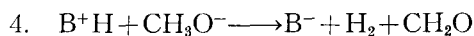
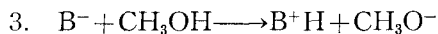
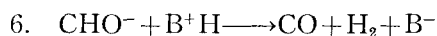
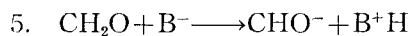


Fig. 1. The yield of gaseous products in the presence of catalysts poisoned with Hammett indicators.

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and similarly for the formaldehyde :



If the above scheme holds for methanol conversion the adsorption of Hammett indicators on surface basic sites of MgO should consequently result in a considerable decrease of activity. In this work, *p*-chloroaniline ($\text{pK}_a = 26.5$) and *m*-dinitrobenzene ($\text{pK}_a = 18$) were adsorbed on MgO surface, the latter indicator being additionally a poison of relatively strong one-electron donor sites.¹⁵⁾ Fig. 1 shows the variation of the yield of gaseous products of methanol conversion (carbon monoxide and hydrogen) with space volume of the substrate as found for pure and indicator containing preparations of MgO precalcined at 550°C. The yield of gaseous products obtained over poisoned catalysts as compared with that over pure MgO amounted to about 50% of the latter and was independent of the type of the poison used and the space volume.

The reaction was also carried out over magnesia rinsed with benzene (the solvent used for preparation of solution of Hammett indicators) which exhibited similar activity to that of pure magnesia. Thus it can be inferred that the decrease in activity of the catalyst results from suppressing the basic sites at $\text{H}_- \geq 18$. Furthermore, in view of the similar yield of gaseous products obtained with both poisoned catalysts it can be concluded that the active sites involved in methanol conversion are those at strengths of $26.5 \leq \text{H}_- < 33$ because only these sites are effectively blocked by the two indicators used. The one-electron donor sites may be ruled out as active in the reaction on the grounds of similarity of degrees of conversion to gaseous products achieved with MgO doped either with *p*-chloroaniline or *m*-dinitrobenzene, the latter substance being a poison of both basic and one-electron donor sites.

The remaining activity of poisoned MgO catalysts may be due to basic sites at $\text{H}_- < 18$, which are not poisoned by the indicators employed or to acid sites of MgO, which however seems considerably less probable.

Coexistence of basic and one-electron donor sites

Basic or one-electron donor properties of alkali metal oxides are generally ascribed to oxygen anions O^{2-} of low coordination. So far it has not been recognized whether the same surface anion may simultaneously play the role

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of either one-electron or two-electron donor. From the results reported by Cordischi and Indovina¹⁶⁾ it follows that strong basic oxide surface should as well exhibit strong one-electron donor properties. The finding Cordischi and Indovina was confirmed by us for a series of MgO-NaOH catalytic systems. The catalyst containing 0.35 mmole Na⁺/g MgO possessed the greatest number of both basic and one-electron donor sites.^{10,17)} Our interest was focused on the question of origin of both types of sites. The fact that the concentrations of one-electron donor sites were markedly lower (*ca.* 0.1 mmole/g) than those of basic sites (1~3 mmole/g) was the first premise in favour of different origin of the two types of sites. The absence of ESR signals of anion radicals or radicals upon adsorption of Hammett indicators on the catalyst surface is the evidence that the colour change of an indicator is solely due to accepting an electron pair and not one electron.

In order to definitely elucidate whether the basic and one-electron donor sites can be attributed to the same or entirely different species of the surface, 2, 4, 6-trinitroaniline was adsorbed on the surface of the catalyst containing 0.35 mmol Na⁺/g MgO; 2, 4, 6-trinitroaniline is a Hammett indicator with the pK_a value equal 12.2. The amount of the indicator was stoichiometric with respect to that of detected basic sites at H_a ≥ 12.2. Upon adsorption of 2, 4, 6-trinitroaniline the catalyst was treated with tetracyanoethylene (TCNE) the known one-electron acceptor. The ESR measurements showed that the concentration of (TCNE)⁻ anion radicals formed on the catalyst surface was comparable with that detected for entirely pure catalyst. Hence it can be ascertained that basic and one-electron donor sites coexist independently on the surfaces of the series of catalysts studied. Only an insignificant number of centres may exhibit the one- and two-electron donor properties.

The present paper concerns exclusively the application of our method to the investigation of solid bases. However it may as well prove useful in studies of solid acidic catalysts. The versatility of the method consists in its applicability both to catalysts with extreme and moderate acid-base properties. Moreover, the adaptability of the method to elevated temperature brings the investigation of physicochemical properties of catalysts near the real conditions of catalytic processes.

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