

## Temperature-Programmed Techniques in Catalysis\*

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The possibilities of application of TPR, TPO, TPD and TPSR techniques in the studies of catalysts as well as in the study of acidity of catalysts' surface are discussed.

**Key words:** temperature-programmed reduction (TPR), oxidation (TPO), desorption (TPD), acidity of catalyst's surface

Temperature-programmed techniques have been the most widely used methods in characterizing chosen properties of catalysts. In literature it is difficult to find a generally adopted definition of the methods. However, the definition of thermal analysis formed by International Conference of Thermal Analysis (ICTA) [1] in 1979 seems adequate. According to it, thermal analysis is a group of techniques, in which physical properties of substance or products of reaction taking place are measured as a function of temperature, while the substance studied is undergoing a controlled program of temperature change. Although physical and physicochemical methods have contributed to the development of our knowledge about physicochemical surface, heterogeneous catalysts cannot be studied with their use in the conditions similar to those, in which real catalytic reactions occur. Using temperature-programmed techniques does not involve vacuum, what is more the research can be done under higher pressure. The method of temperature-programmed desorption (TPD) was used for the first time by Amenomiya and Cvetanovic in 1967 [2,3]. Initially it was employed mainly in the study of industrial catalysts in conditions similar to catalytic processes used in industry. This technique was developed further and has been widely used in research laboratories as well for the last 25 years. Apart from TPD, the following methods are commonly used: TPR (temperature-programmed reduction), TPO (temperature-programmed oxidation) and TPSR (temperature-programmed surface reaction).

Figure 1 shows the degree of using different techniques for physicochemical characterization of catalysts and for studies of catalytic reactions. Methods using programmed temperature rise (TPD, TPR, TPO, TPSR) are among those commonly used. They are relatively cheap, fast and experimentally simple, often automated recently. Altamira apparatuses AMI-1, AMI-3 working with a computer and an appara-

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\*Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

tus called “Peak”, designed in the Institute of General and Ecological Chemistry of Technical University in Łódź, enable obtaining information unavailable in the measurements carried out in static conditions, because here temperature as well as surface coverage change in time. Temperature-programmed techniques are particularly useful in the study of interactions between reactants and catalyst’s surface including catalytic reaction [4,5] as well as adsorption of gases on metals and metal oxides [6–10].

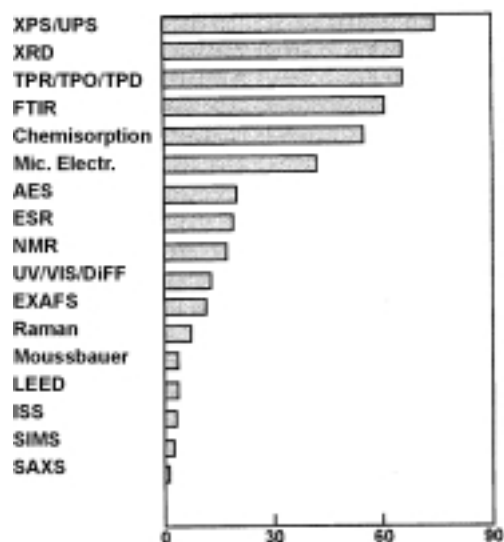


Figure 1. More important techniques used in catalysis in the last years.

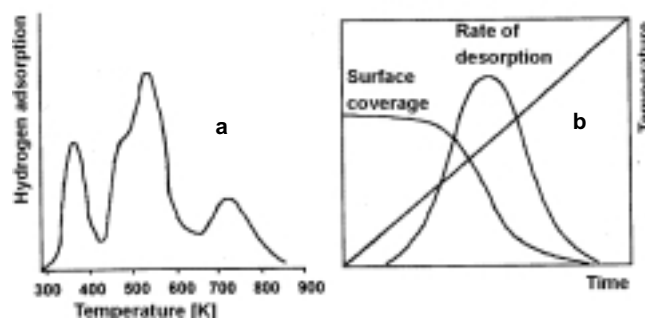


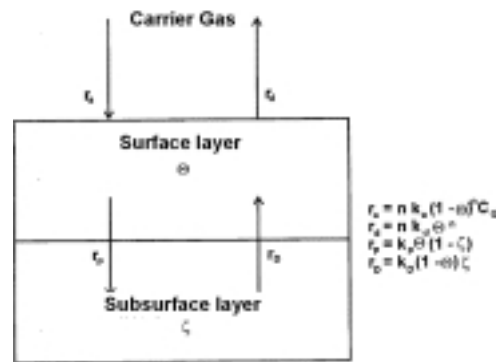
Figure 2. A typical course of TPR (a) and TPD (b) [11].

Figure 2 presents typical courses of TPD and TPR [11]. These are classical non-equilibrium processes with a large number of variables. Temperature of maximum peak proves the strength with which a reactant (adsorbate) interacts with the surface of solid. The stronger the bond, the higher the temperature of peak desorption.

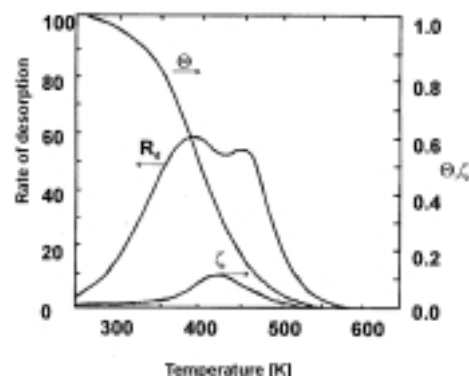
There are four basic models of kinetics of desorption [12]: – primary kinetics excluding readsorption, – secondary kinetics excluding readsorption, – primary kinetics including readsorption, – secondary kinetics including readsorption.

Heterogeneity of surface plays a significant role in the course of TPD and determines the number of peaks. If heat of adsorption of reactants on adsorptive catalytic centres differs considerably, in the course of TPD one peak for each type of adsorptive centres is observed. However, it is not absolutely reliable, as apart from heterogeneity of surface other factors influence the shape and position of peaks. The most important ones are: – mass transfer, that is inner and outer diffusion which delays the course of experimental curves in time, – subsurface diffusion and adsorption, – readsorption, – kinetics of desorption.

There exist many articles on theoretical analysis, mathematical model and simulation of TPD, TPR, TPO, and TPSR processes [13–19]. Different types of mathematical models from simple monocomponent adsorption to multicomponent adsorption, subsurface diffusion, surface reaction and order of process for homo- and heterogeneous surfaces have been developed.



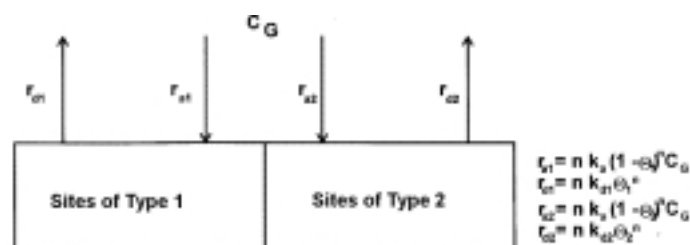
**Figure 3.** Energy homogeneous surface. TPD/TPR schemes during which processes of readsorption and subsurface diffusion play an important role [14].



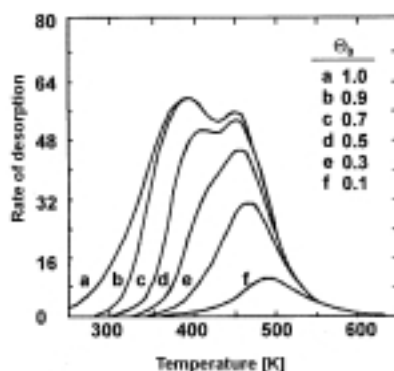
**Figure 4.** Energy homogeneous surface. Simulation of TPD profiles with the use of a model of subsurface diffusion. The figure shows changes in surface coverage [14].

There exists a large number of derived equations for different conditions, in which the process is carried out [11]. Figures 3 and 4 show a theoretical exemplary course of TPD for homogeneous surface [14]. The model presents readsorption and sub-

surface diffusion. Fig. 4 shows clearly 2 peaks, the second one being connected with desorption of adsorbate from a subsurface layer, not from adsorptive centres of higher binding energy.

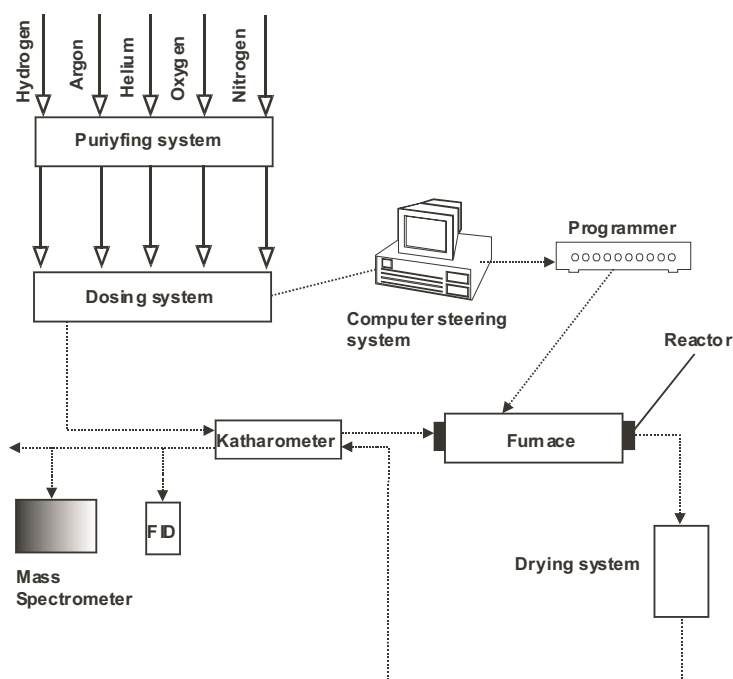


**Figure 5.** The scheme of temperature-programmed desorption from a catalyst with two adsorptive centers with different binding energies [14].



**Figure 6.** The simulated course of TPD for a catalyst with two different energy centres for various degrees of coverage [14].

Figures 5 and 6 show a model and course of TPD for a catalyst with two different energy centres of different degrees of coverage. Temperature-programmed techniques are used in a variety of heterogeneous studies such as: – determination of binding energy of reactant (adsorbate) particles with catalyst's surface; – determination of selective surface of metals and their dispersion; – determination of acidity of catalyst's surface; – determination of susceptibility of systems to reduction or oxidation and determination of different stages of reduction or oxidation (ionic valence); – determination of resistance of system to temperature in different atmospheres; – characterization of stage of reduction and calcination in the process of catalyst's preparation; – determination of interaction between components of catalysts: • metal-metal (alloy), • study of SMSI effect, • study of spillover effect; – study of catalysts' deactivation; – determination of optimal conditions of catalysts' regeneration; – study of carbon deposit; – study of catalytic reaction (TPSR), e.g. methanization, hydrogenation, oxidation and others.



**Figure 7.** The scheme of the system used in temperature-programmed techniques.

Figure 7 shows the basic scheme of apparatus, which is used in temperature-programmed techniques. Major elements of apparatus are: a reactor, temperature-programmed furnace, purifying system and a dosage system for carrier gas and reactant gases, a system for chemical analysis. An universal detector in TPD, TPR and TPO is a katharometer, however, a mass spectrometer becomes more and more often used, and in the case of temperature-programmed surface reaction other selective detectors are also used, mainly FID flame-ionization detector. In temperature-programmed techniques the shape and position of peaks depend on many factors, which should be taken into account in the experiment, in order to decrease all diffuse effects in the first place, but also subsurface diffusion, adsorption and readsorption.

Therefore, very important parameters, which must be optimized in temperature-programmed techniques, are: – rate of flow of carrier gas, – ration of reactant gas to inert gas, – volume of sample and mass catalyst, – size of catalyst's particles, – geometry of reactant vessel, – intensity of signals (type of detector), – pressure system.

Monti and Baker [20] proposed the use of characteristic K number for TPR to obtain optimal conditions of reduction. The K value is connected with the rate of heating, concentration of hydrogen, overall rate of gas flow, size of reduced sample; in other words parameters, that can be easily adjusted. K value was defined in the following way:

$$K = \frac{S_i^0}{c_g \times F_0}$$

where:  $c_g$  – concentration of hydrogen when entering the reactor [ $\text{mol}/\text{m}^3$ ];  $F_0$  – space velocity of flow of reducing gas [ $\text{m}^3/\text{s}$ ];  $s_i^0$  – initial concentration of reduceable “i” compounds on the surface.  $K$  value should be in the range of  $55 < K < 140$  [s]. In most cases measurements are carried out under atmospheric pressure, however, higher pressures can be used as well [21]. Experimental conditions used in temperature-programmed techniques are presented in Table 1.

**Table 1.** Experimental conditions used in temperature-programmed techniques (mainly metallic catalysts supported on carriers) [11].

	<b>TPD</b>	<b>TPR</b>	<b>TPO</b>	<b>TPSR</b>
Carrier Gas	Highly pure helium, nitrogen, argon	Highly pure nitrogen	Highly pure helium, nitrogen	Highly pure helium, nitrogen hydrogen
Rate of flow [ $\text{cm}^3/\text{min}$ ]	15–60	15–30	30–90	30–60
Adsorbate, reactant	hydrogen	nitrogen + 5% $\text{H}_2$	Helium (nitrogen) + 5% $\text{O}_2$	Reaction dependent
Mass of catalyst [mg]	100–500	100–500	100–500	100–500
Size of particles [mm]	0.025–0.25	0.025–0.25	0.025–0.25	0.05–0.5
Type of reactor	Quartz pipe	Quartz pipe	Quartz pipe	Quartz pipe
Rate of heating [K/min]	10–60	4–60	10–60	10–60
Type of detector	Katharometer, mass spectrometer	Katharometer	Katharometer, mass spectrometer	Flame-ionization katharometer, mass spectrometer, selective detectors
Pretreatment	Catalyst dependent	Catalyst dependent	Catalyst dependent	Catalyst and reaction dependent

A typical temperature-programmed measurement usually follows such stages: – pretreatment of catalyst (desorption of adsorbed gases, reduction), – purification of catalyst’s surface by flow of pure carrier gas at determined temperature, – submission of sample to reactant gas, – desorption of part of physically adsorbed adsorbate, – heating of sample with linear rise in temperature as a result of which adsorbed particles are carried in the stream of carrier gas and then registered, – analysis of desorbed particles with the use of a detector (gas chromatography, mass spectroscopy).

#### Exemplary uses of TPD, TPR and TPO

Temperature-programmed techniques are especially useful in the study of interactions between a tested particle and a catalyst’s surface. The interaction between oxygen and the catalyst’s surface was studied most often, due to the practical possibilities of those catalysts in catalytic oxidation of olefins [4,5,22–25]. The ability of oxide catalysts to total or selective oxidation of olefins is connected with the kind of

reactant oxide in the catalyst [26,27,28]. According to TPD studies metal oxides can be divided into three groups (Table 2), including oxygen adsorption and desorption [22].

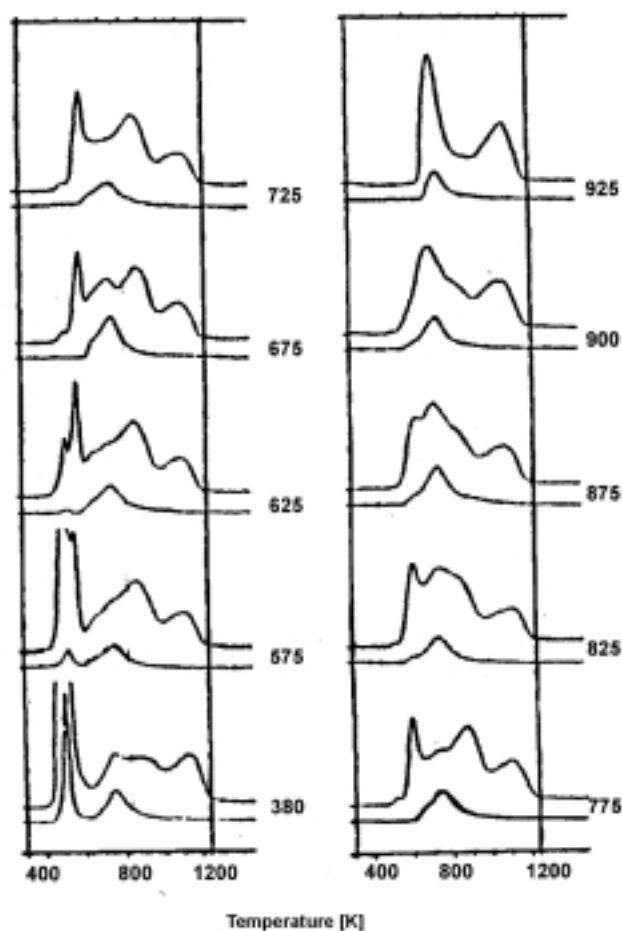
**Table 2.** Desorption of oxygen from different metal oxides [22].

Group	oxide	T <sub>m</sub> (K)	V(cm <sup>3</sup> /m <sup>2</sup> )
A	V <sub>2</sub> O <sub>5</sub>	–	0
	MoO <sub>3</sub>	–	0
	Bi <sub>2</sub> O <sub>3</sub>	–	0
	WO <sub>3</sub>	–	0
	Bi <sub>2</sub> O <sub>3</sub> -2MoO <sub>3</sub>	–	0
B	Cr <sub>2</sub> O <sub>3</sub>	723	2.13×10 <sup>-2</sup>
	MnO <sub>2</sub>	323 543 633 813	6.54×10 <sup>-2</sup>
	Fe <sub>2</sub> O <sub>3</sub>	328 623 758	4.05×10 <sup>-3</sup>
	Co <sub>3</sub> O <sub>4</sub>	30 438 653	3.30×10 <sup>-2</sup>
	NiO	303 608 698 823	1.12×10 <sup>-2</sup>
	CuO	398 663	1.42×10
C	Al <sub>2</sub> O <sub>3</sub>	338	2.04×10 <sup>-4</sup>
	SiO <sub>2</sub>	383	2.99×10 <sup>-5</sup>
	TiO <sub>2</sub>	398 463 593	2.52×10 <sup>-5</sup>
	ZnO	463 593	2.45×10 <sup>-4</sup>
	SnO <sub>2</sub>	353 423	2.11×10 <sup>-3</sup>

A – metal oxides which do not adsorb or desorb oxygen in the temperature range 283–833 K, B – metal oxides which give relatively large amounts of desorbed oxygen, C – metal oxides for which removal of oxygen at high temperatures and next its adsorption at a relatively low temperature give small desorption of oxygen in the temperature range 283–673 K.

The amount of desorbed oxygen for B and C oxides up to 833 K makes only a few percent of surface coverage of a sample. It may lead to the conclusion that sites of oxygen adsorption are connected with defects of the surface. TPD studies proved that oxides of group A, which are selective oxidation catalysts, do not show noticeable desorption of oxygen. On the contrary, oxides of group B adsorb considerable amounts of oxygen, which are characterized by total oxidation of olefins [29]. Oxides of group C stand in between. They adsorb moderate amounts of oxygen and catalyze both the selective and the total oxidation of olefins. It shows that total oxidation is connected with adsorbed oxygen, whereas oxygen of catalyst's lattice plays an essential part during selective oxidation [16]. Molybdenum-bismuth catalysts (Bi<sub>2</sub>MoO<sub>6</sub>) were characterized using TPO method [23]. Two peaks were found: low-temperature at 431 K, which is a result of oxidation of Mo<sup>4+</sup> to Mo<sup>6+</sup> and Bi<sup>0</sup> to Bi<sup>m+</sup>, where 0 < m<sup>+</sup> < 3, and high-temperature at 613 K, which is related to oxidation of Bi<sup>m+</sup> to Bi<sup>3+</sup>. The use of TPR method showed that the high-temperature peak is connected with oxidation of propylene to acrolein. Catalysts CoO-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and NiO-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [30–32]

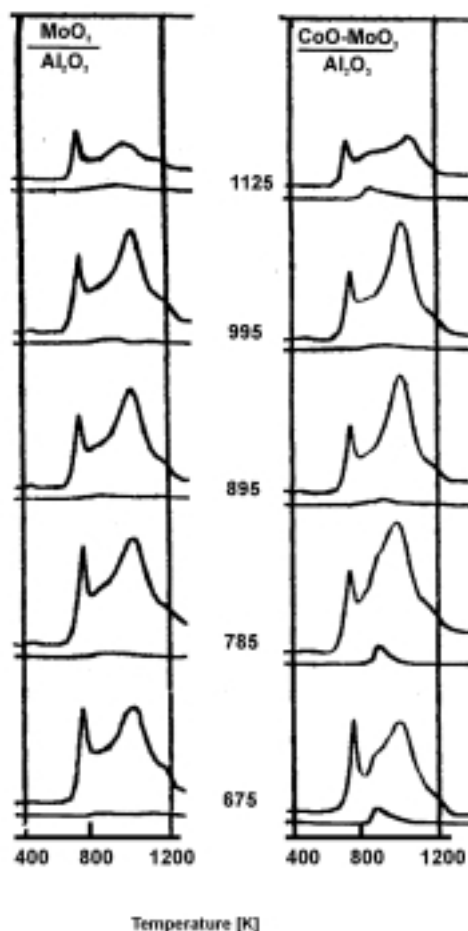
were studied very thoroughly with the use of temperature-programmed methods, because these catalysts are much more active in the reaction of hydrodesulfurization, and hydrocracking than monooxide catalysts like  $\text{CoO}/\text{Al}_2\text{O}_3$ ,  $\text{NiO}/\text{Al}_2\text{O}_3$ , and  $\text{MoO}_3/\text{Al}_2\text{O}_3$ . It turned out that, for example, Co in those catalysts does not influence the reduction of  $\text{Mo}^{6+}$  ions, while the presence of molybdenum has a promoting impact on the reduction of  $\text{Co}^{2+}$  ions. Strong Co-Mo interaction has an influence on reduction temperature – it decreases from 1200 K in  $\text{CoO}/\text{Al}_2\text{O}_3$  to 800–850 K for  $\text{Co-MoO}_3/\text{Al}_2\text{O}_3$ . The studies proved an active role of Co in HDS catalysts, whereas Mo promotes mainly the activity of Co through decreasing the interaction between Co ion and  $\text{Al}_2\text{O}_3$  carrier.



**Figure 8.** The course of TPR for 9.1%  $\text{CoO}/\text{Al}_2\text{O}_3$  catalysts calcinated at different temperatures. Above the course of indication of katharometric detector, below FID indication [30].

Figure 8 presents the course of TPR 9.1%  $\text{CoO}/\text{Al}_2\text{O}_3$ , and Figure 9 shows the course of TPR for  $\text{MoO}_3/\text{Al}_2\text{O}_3$  and  $\text{CoO-MoO}_2/\text{Al}_2\text{O}_3$  as a function of calcination temperature [30].





**Figure 9.** The course of TPR for MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and CoO-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> as a function of calcination temperature [30].

TPR method proved that the interaction of different carriers with metal ions modifies the temperature of reduction. Thus, the reduction (TPR) and desorption (TPD) can take place at lower or higher temperature, depending on the interaction between metal oxide and carrier. It is illustrated by Fig. 10 for metal oxide supported on Al<sub>2</sub>O<sub>3</sub> and in mechanical mixture of NiO and Al<sub>2</sub>O<sub>3</sub> [33].

TPR profiles in Figures 11 and 12 show that the reduction of CeO<sub>2</sub>, supported on Al<sub>2</sub>O<sub>3</sub> with the use of an impregnation method, differs significantly from the reduction of oxide remaining in the mechanical mixture with Al<sub>2</sub>O<sub>3</sub> [34].

For the mechanical mixture of CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> a mutual interaction between components is not observed, even during high-temperature oxidation and reduction. However, in the reduction of CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> systems, obtained with the use of an impregnation method, CeAlO<sub>3</sub> is formed. Ce(III) connected with Al<sub>2</sub>O<sub>3</sub> in the structure of CeAlO<sub>3</sub> is more resistant to oxidation than Ce<sub>2</sub>O<sub>3</sub>.

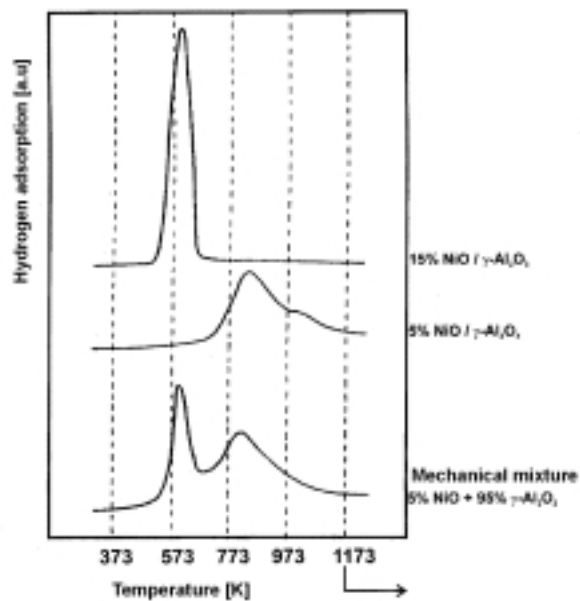


Figure 10. TPR profiles for NiO/Al<sub>2</sub>O<sub>3</sub> [33].

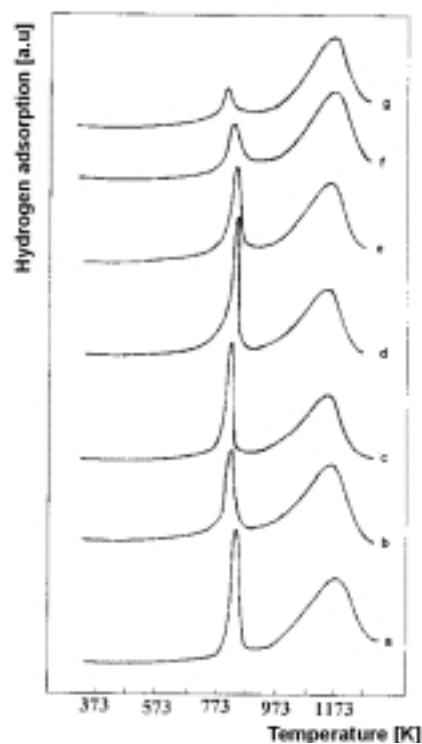
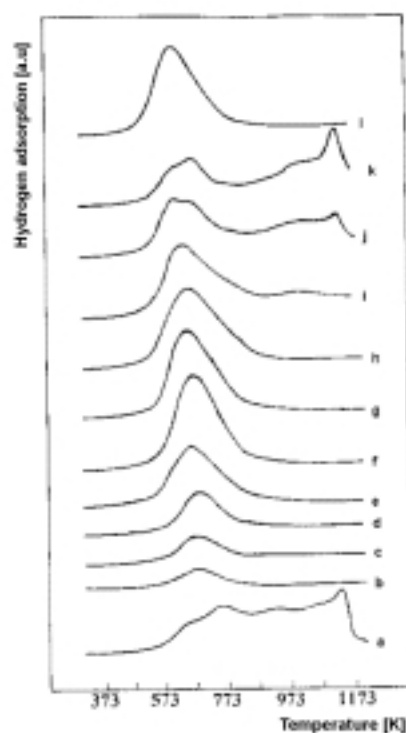


Figure 11. TPR profiles of mechanical mixture 10CeO<sub>2</sub> + 90Al<sub>2</sub>O<sub>3</sub>: a) the profile of initial sample, b–g) profiles after the reoxidation of reduced sample at temperatures 293, 473, 673, 873, 1073 and 1173 K, respectively [34].

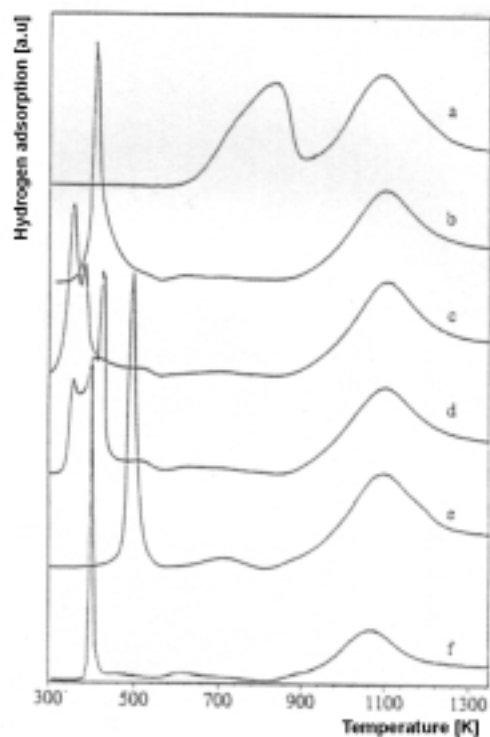


**Figure 12.** TPR profiles of  $10\text{CeO}_2/90\text{Al}_2\text{O}_3$ : a) the profile of initial sample, b–l) profiles after the reoxidation of reduced sample at temperatures 293, 373, 473, 573, 673, 773, 873, 973, 1073 and 1173 K and again 673 K, respectively [34].

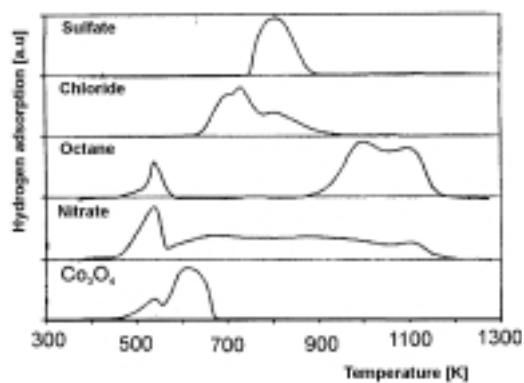
The TPR method was also used to study the influence of different noble metals on reducibility of  $\text{CeO}_2$ . Fig. 13 shows how much the presence of noble metals modifies the TPR profile [35].

Profile (a) shows the reduction of  $\text{CeO}_2$ . The first low-temperature peak stands for the most easily reduceable surface atoms of oxygen. The second peak refers to the reduction of  $\text{CeO}_2$  in mass. An addition of even small amounts of noble metal promotes effectively the reduction of surface  $\text{CeO}_2$ , which is proved by the displacement of the low-temperature peak. The new peak at low temperatures stands for the reduction of noble metal. The amount of hydrogen adsorbed in this process is usually higher than the amount required for the reduction of oxide metal precursor. It means that the reduction of surface  $\text{Ce}^{4+}$  also occurs at very low temperatures, which can indicate the course of the process of hydrogen spillover.

TPR, TPD and TPO can be leading methods in choosing conditions of preparation of metallic and oxide catalysts supported on carriers. Generally speaking, the sample will show a very characteristic course of TPR, which can be used as a “finger print”. Obviously, reproducing such a “finger print”, constant experimental conditions must be created. Therefore, a one can use TPR as a quality test to check the reproducibility



**Figure 13.** TPR profiles: a)  $\text{CeO}_2$ , b)  $\text{Rh/CeO}_2$ , c)  $\text{Ir/CeO}_2$ , d)  $\text{Ru/CeO}_2$ , e)  $\text{Pt/CeO}_2$ , f)  $\text{Pd/CeO}_2$  [35].



**Figure 14.** The influence of kind of anion on the TPR course for 9%  $\text{Co/SiO}_2$  and  $\text{Co}_3\text{O}_4$  catalysts. Impregnated catalysts were dried at 373 K, and calcinated at 673 K, in the atmosphere of air for 1 hour.

of preparation of catalysts' precursor. On the contrary, one can easily see, which variable of catalyst's preparation will really influence its properties. Fig. 14 shows an influence of the kind of anion on the course of TPR for 9%  $\text{Co/SiO}_2$  catalyst and  $\text{Co}_3\text{O}_4$ .

Figure 15 presents the influence of the type of carriers, produced by different Firms, on the course of TPR 3% Fe/ZrO<sub>2</sub>.

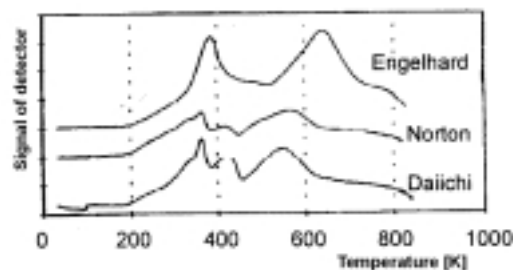


Figure 15. TPR 3% Fe/ZrO<sub>2</sub> (carriers produced by different Firms).

### Temperature-programmed surface reaction TPRS

In order to carry out a temperature-programmed surface reaction, two reactants are adsorbed simultaneously or successively and next the temperature-programmed heating in an inert gas takes place. Another possibility is that one reactant is adsorbed and the second is a carrier gas or is part of it. A lot of information can be obtained from TPRS experiment if all the products of the process are analysed [36–42]. There may be centres of different activity on the catalyst's surface. Programmed rise in temperature causes changes in their activity and, thus, changes the catalyst's properties. Such changes cannot be expected in measurements in static kinetics. TPRS was used to study oxidation of methanol on MoO<sub>3</sub> among others. After the adsorption of methanol, followed by TPD, two thermodesorptive peaks were obtained: a low-temperature peak, consisting of methanol only ( $T_{\max}$  393 K) and the second peak ( $T_{\max}$  493 K) made up of formaldehyde, methanol and water [18] (Fig. 16).

Carbon deposit is a very important problem, both in industry and elemental studies [43]. A lot of effort is put into creating catalysts, resistant to the formation of car-

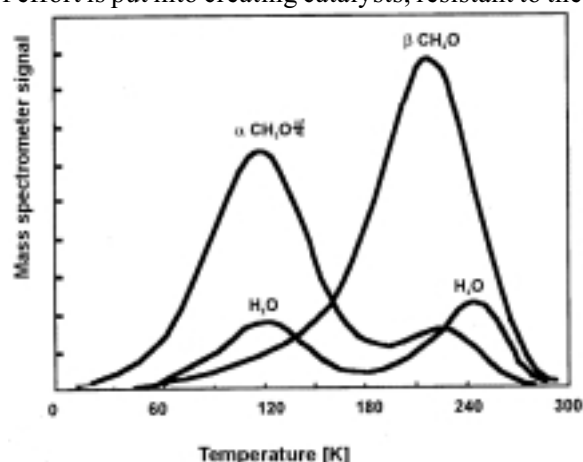
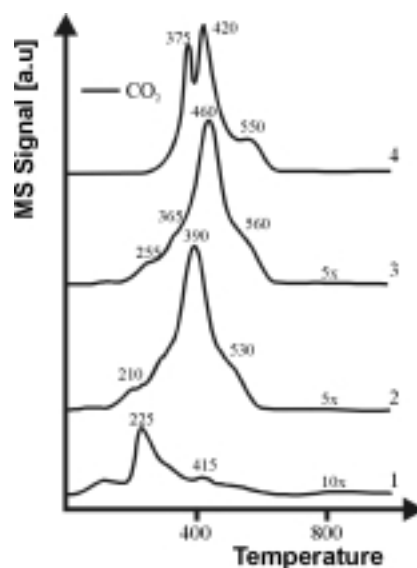


Figure 16. The course of thermodesorption of methanol with MoO<sub>3</sub> [18].



**Figure 17.** TPO profile of 9.3% Co/Al<sub>2</sub>O<sub>3</sub> catalyst coked in propane cracking at: 1 – 300°C/2 h, 2 – 350°C/2 h, 3 – 350°C/6 h, 4 – 400°C/1 h [44].

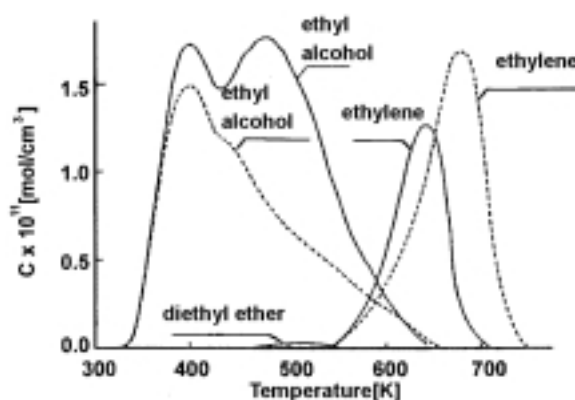
bon deposit. This appears, when we deal with heterogeneous catalysts in contact with organic substances at higher temperatures. The deposit exists in the form of fibrons of amorphous carbon or graphite. To understand better the mechanism of coke's precipitation, different techniques are used to characterize the carbon formed. One of them is temperature-programmed hydrogenization (TPH), that is the reaction of carbon deposit with hydrogen or temperature-programmed oxidation  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (TPO).

Figure 17 shows TPO profiles for Co/AlO<sub>3</sub> system, coked in the reaction of propane cracking, on which four stages of removal of carbon deposit are observed. The maxima of carbon emission occurred between 210–255°C, 365–390°C and 530–560°C. It was noticed that the maxima of CO<sub>2</sub> emission move towards higher temperatures with the rise in temperature and time of coking. This effect is ascribed to the changes in the structure of carbon deposit.

#### **The use of temperature-programmed techniques in determination of acidity of catalyst's surface**

The catalytic activity of a large group of catalysts used in cracking, hydrocracking, isomerization, polymerization of alkenes, dehydration of alcohols and many other processes is due to the acidity of their surfaces. Knowledge of the number and strength of acid sites, and also the type of acidity (Brönsted and Lewis) involved, is extremely important as it helps to explain the mechanism of reactions occurring at the surface of these catalysts for given reactions [45]. Different methods of studying acidity of the surface of solids were worked out. The most important ones are: 1) base titration (*e.g.* butylamina) in the presence of acid-base indicators; 2) microcalorimeter measurements of base adsorption; 3) measurements of thermo-programmed base desorption (*e.g.* ammonia), 4) IR spectroscopic studies of ammonia adsorption or pyridine [46].

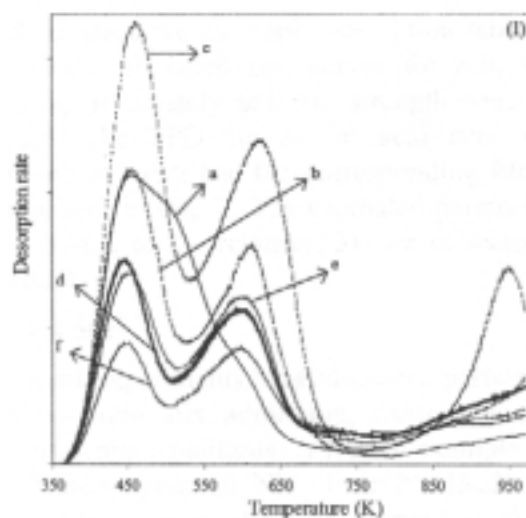
Figure 18 shows TPSR of ethanol from fresh and poisoned with sodium  $\gamma\text{-Al}_2\text{O}_3$  [47]. The fresh catalyst gives two peaks. They correspond with the heterogeneity of  $\gamma\text{-Al}_2\text{O}_3$  surface with Brönsted and Lewis acid sites of different strength of acidity. The interaction of alcohol hydroxyl groups is different with surface hydroxyl groups and with Lewis sites. The impregnation of the catalyst with sodium proves poisoning stronger Brönsted's and Lewis acid centres. The first peak is smaller and the second (490 K) almost disappears, when the catalyst is poisoned. It is worth noticing, that TPSR is a very useful technique in the studies of rate of reaction on different centres, which is difficult or impossible in the case of most conventional methods. TPSR appeared to be of much use in the studies of catalyst's deactivation and kinetics.



**Figure 18.** The curves of thermodesorption of ethanol and ethylene with  $\gamma\text{-Al}_2\text{O}_3$ : — level of poisoning 0% Na, ---- level of poisoning 1.5% Na [47].

Acidity is also one of the most important characteristics of zeolites [48], which makes them very useful in acid catalysis. Catalytic properties, such as activity and selectivity, depend not only on the number of acid sites, but also on their specific activities. It is clear that this activity is related to the acid strength of the intervening sites.

Temperature-programmed desorption (TPD) of ammonia is one of the major methods being used and some authors have proposed a numerical procedure to perform digital deconvolution of the curves obtained by single TPD experiment into the related mono-energetic component curves [49]. Costa *et al.* [50] characterized the acid site strength distribution of several ZSM-5 catalysts with different Si/Al ratio and different protonic content, applying the above mentioned deconvolution method on ammonia TPD curves. These results were then correlated with the results for the catalytic activity for n-heptane transformation, using the same type of Brönsted equation. It can be noticed that for most catalysts two main bands can be observed, which show a maximum in desorption rate around 450 and 630 K, in good agreement with other previous reports [51,52]. As the Si/Al ratio increases, the total number of acid sites decreases, so it would then be expected that the area below the TPD curve should also decrease.



**Figure 19.** TPD of  $\text{NH}_3$  thermograms from the catalysts with different Si/Al ratio: (a) ZSM5/19; (b) ZSM5/26; (c) ZSM5/29; (d) ZSM5/40; (e) ZSM5/42; (f) ZSM5/127 [49].

Nevertheless, this is not what can be observed in Fig. 19. For instance, the TPD curve for ZSM5 (Si/Al = 29) is the one with the higher area. This fact is in good agreement with the activity of this catalyst towards n-heptane transformation, which means that there are factors other than the Si/Al ratio that lead to different acidity in ZSM-5 samples. A nonlinear decrease in the number of acid sites, when the Si/Al ratio value increases, has been already reported by other authors for ZSM-5 [53]. Using the digital deconvolution method Costa *et al.* [49] could determine the acid site strength distribution for each catalyst as a function of the activation energy for ammonia desorption from a single TPD experiment. Assuming that the activation energy for ammonia desorption can be used as a direct measurement of the acid strength and, again, that there is no significant interaction between sites with different energy, Brønsted-type equations can be applied for the ensemble of acid sites with the same activation energy for ammonia desorption. The activation energy for  $\text{NH}_3$  desorption allows an adequate description of the acid site strength distribution, that can be quantitatively correlated with the catalytic activity of different zeolites. This means, that the activation energy for ammonia desorption can be used as a practical scale for zeolites samples with a catalytic meaning. A systematic approach to these Brønsted-type relationships for several acid catalysts and different reactions can be envisaged, so that a fast way to analyse and develop new catalysts could be used in acid catalysis by solids.

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