THE USE OF THERMAL ANALYSIS TECHNIQUES

IN HETEROGENEOUS CATALYSIS

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Abstract

This review surveys recent developments in thermal analysis techniques
applied in heterogeneous catalysis. These techniques can be used in catalytic
investigations as a tool for characterization of catalysts. Thermal analysis in
catalysis comprises the measurement of heat evolved during a reaction over
a catalyst and the use of heat for determining the reduction or sorption
capability of a catalyst. A variety of instruments were developed and are in
development now, because the applications are numerous and different.

Temperature programmed reduction and temperature programmed
desorption have been used in many laboratories. Techniques such as
temperature-programmed reaction spectroscopy and differential scanning
calorimetry are gaining more and more interest.

Introduction

In this article an outline of various applications of thermal analysis methods
to study catalysis is given. Thermal analysis techniques are extremely useful
in studying catalysts and to characterize surface species. Thermal analysis
may be used in the preparation, characterization and application of
catalysts. The methods most applied for characterization are temperature-
programmed desorption (TPD) or decomposition and temperature-
programmed reduction (TPR). Temperature-programmed techniques are
relatively simple and inexpensive. They are very similar to each other and
the apparatus used is practically identical.

TPD provides information about the stoichiometry of transformations of
clusters present on the surface of the catalyst, whereas TPR informs us about
the oxidation state and/or states of surface metal species.

The TPD technique accompanied by a chemical reaction has gained
increasing interest. Temperature-programmed oxidation (TPO), reduction
(TPR), sulphidation (TPS), methanation (TPM) and denitrification (TPN) are
common practice in catalysis. These methods fall in the category of tempera-
ture-programmed reaction spectroscopy (TPRS) [1]. This is a method in

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which a reactive gas or gas mixture flows over the catalyst during linear temperature programming.

TPR has become one of the most widely used physicochemical techniques for the characterization of heterogeneous catalysts. It has been used to study the rate and extent of hydrogen uptake. TPR is a convenient technique for following the evolution of a catalyst system as a function of the preparation of the precursor and the calcination conditions.

Chemisorption and temperature-programmed desorption are useful techniques for studying the interaction of gases with catalyst surfaces. TPD combined with other methods such as mass spectrometry, gas chromatography, Mössbauer spectroscopy or X-Ray diffraction, is useful for studying metal-support interactions, activation and deactivation processes, influence of promotors etc. The extent of metal-support interaction is correlated with the reducibility of the metal component. Strong metal-support interaction is generally associated with low reducibility of the metal component.

DSC is used to study the calcination of catalysts as well as to determine the kinetics of reactions such as methanation and dentrification.

The present review covers the period in Chemical Abstracts from August 1985, after the 8th ICTA Conference, until August 1988, including the proceedings of the 9th ICTA Conference.

Each of the topics discussed deserves far more attention than it receives in this review, which is restricted in its scope because of the limited time and space available.

The emphasis is on: methanation [2-7], bimetallic catalysts [8-11], decomposition reactions [12-15], temperature-programmed reaction spectroscopy [3-5,12,16-21], zeolites [22-25], metal-support interaction [26-29] and carbonaceous deposits [30-32]. In a number of studies attention is focused on the analysis technique itself [33-35]. The final section deals with a variety of studies. Catalysts such as CuO on carbon [36], Co_3O_4 [37], Pt on Al_2O_3 [38], Pd on SiO_2 [39], Pd/V_2O_5 [40], Mo_2C [41], Fe_2O_3 on Al_2O_3 [42], CoO on Al_2O_3 [43], Ni on MgO [44] and Ni on Al_2O_3 [45] will be discussed.

Methanation

In methanation CO and H_2 react over a nickel on alumina catalyst to form CH_4.

The paper of Munteanu et al. [2] analyses some results of the methanation of CO on Ni on Al_2O_3 catalysts using a high vacuum TPD technique. The methanation of CO shows a structure sensitivity in the temperature range of 473-673 K. At 673 K the methanation becomes structure-insensitive. In the presence of large nickel particles (5-60 nm) the methanation activity decreases, whereas in the presence of small particles (5-6 nm) the activity increases, at increasing temperature.

Hakvoort et al. [3] studied the nickel-catalyzed methanation of CO by DSC. They used Ni on Al_2O_3 pellets. The use of pellets means that the heat exchange between the sample and the gas phase has to be considered.

Therefore, calibration constants were obtained by heat measurements in combination with the measurement of gas chromatography.

Using the DSC technique Dötsch and Fink [4] demonstrated its possibilities and limitations through the examples of methanation and methanol synthesis. In their paper they showed that the calibration factor can be calculated for small and well-conducting samples. Moreover, the authors pointed out that evolved gas analysis was required for the interpretation of the heat measurements.

Kitchener et al. [5] devised two methods, called temperature-programmed methanation (TPM) and step-TPM as part of the development of methanation catalysts, which combine high activity with a resistance to deactivation by high-temperature sintering. Step-TPM was introduced because of problems arising with TPM. These: (i) the catalyst is hotter than the nominal temperature because of the heat evolved in methanation; (ii) TPM curves are analysed on the assumption that the methanation is highly selective and ignores the possibility of the reverse CO-shift reaction; and (iii) the hydrogen cannot be measured directly, that is, water has been removed from the gas stream the amount of which is dependent on the extent of the reaction.

The interaction of H_2 and CO at Pd on SiO_2, promoted with Li, Na, K, Rb or Cs by using TPD, TPR and temperature-programmed surface reaction (TPSR) was investigated by Rieck and Bell [6]. Promoting the catalyst does not influence the amounts of H_2 and CO adsorbed on the metal but it changes the steady-state activity of the catalysts. The promoted catalysts showed a lower activity for the methanation than the unpromoted catalysts, decreasing in the order: unpromoted $>$ Li $>$ Na $>$ K $>$ Rb $>$ Cs. The catalysts were previously reduced at 573 and 673 K and showed different behaviour with respect to the dissociation of CO. Reduction at 673 K increases CO dissociation of the promoted samples whereas the dissociation occurs less readily after reduction of the catalyst at 573 K.

Kakuta and White [7] studied the desorption of CO and D_2 from Ru on SiO_2 catalysts by UHV-TPD. From these experiments it was deduced that hydrogen spillover occurs at temperatures above 323 K on Ru on SiO_2 catalyst and that there was no spillover of CO on these catalysts. The role of spillover in methanation was thus established.

Bimetallic catalysts

Bimetallic catalysts are attractive systems because of their high stability and selectivity for many reactions. Supported Fe/Rh, Ru/Cu, Pt/Ge and Co/Rh are described in this section.

A modified differential heat flow microcalorimeter (Calvet type) used by Gatte and Phillips [8] allowed simultaneous measurement of both adsorption kinetics and heat evolution dynamics. The calorimeter was used to measure the adsorption of oxygen on a graphite-supported catalyst containing Fe, Rh and Fe/Rh as active material. Their data showed that oxygen adsorption on the Fe on carbon catalyst is a steady high-heat process through a coverage of

approximately 0.75. After this point the heat rapidly falls off until the surface is completely passivated and only physical adsorption occurs. On the rhodium on carbon catalyst this decrease becomes rapid after a coverage of approximately 0.6. In case of the fully reduced (670 K) bimetalic catalyst the heats of adsorption fall between the two monometallic extremes. Furthermore, it was shown that three distinct 'states' of the catalysts can be achieved by different gas-temperature treatments. These states were: the Fe-Rh alloy, segregated α-Fe and τ-Rh and the immiscible oxides Fe_2O_3 and Rh_2O_3 on the carbon support.

A TPR study was conducted by Damiani et al. [9] to investigate the interaction between the metals in the SiO_2 supported Ru/Cu catalysts. Two peaks were found in the TPR spectrum after oxidation at 623 and 773 K, which indicates that oxidized particles of different sizes and/or different composition exist separately on the support.

Another bimetallic catalyst, Pt/Ge on alumina was studied by Goldwasser et al. [10]. The catalysts contained equal amounts of Pt (1% by weight) and had a dispersion which varied between 0.56 and 0.7, with a germanium load varying between 0 and 1%. From the results of this study it was concluded that at a higher Ge load in the catalyst the H_2 uptake increases, whereas the activity in the hydrogenation of benzene decreases. Moreover, at a high Ge content Ge is reduced to Ge^{4+} which influences the electronic properties of platinum. From the results it was concluded that the presence of Ge is not responsible for the formation of small ensembles of platinum but for electronic changes induced by Ge.

Van 't Blik and R. Prins [11] characterized Co/Rh on alumina catalyst using TPO, TPR and TPD techniques. Rhodium in a Co/Rh on alumina catalyst enhances the reducibility of part of the cobalt, but it does not prevent the formation of cobalt aluminate. TPR results demonstrated that bimetallic particles were formed during reduction of the precursors of the catalyst. The inner and outer shells of the bimetallic particles are enriched with Re and Co respectively. During the oxidation of the reduced catalyst at room temperature cobalt is oxidized in larger measure while rhodium remains metallic. The oxides Co_3O_4 and Rh_2O_3 segregate after oxidation at 773 K. However, the Rh/Co on TiO_2 showed no segregation, which is probably due to a cobalt rhodate phase that was formed [11a]. After reduction and thorough oxidation at 773 K of the catalyst metal oxide particles were formed close to each other. The same results were found for the Co/Rh on SiO_2 catalysts [11b].

Decomposition reactions

Fubini et al. [12] applied DSC to study monophasic nonstoichiometric spinel-type Zn/Cr catalysts formed by coprecipitation of their nitrates. At temperatures above 753 K these catalysts decompose into a biphasic solid consisting of ZnO and $ZnCr_2O_4$, the latter being catalytically inactive in the methanol decomposition and CO adsorption. The nonstoichiometric catalyst showed an enhanced chemisorptive capacity towards CO and an increase in

methanol decomposition. These two processes, the adsorption of CO and the decomposition of methanol, were ascribed to the presence in the catalyst of Cr^{3+} and Zn^{2+}.

The adsorption and decomposition of 1-propanol, 1-butanol, and 2-butanol on polycrystalline ZnO were determined on the basis of TPD by Bowker et al. [13]. The alcohols decompose in two steps namely by α-C-H bond scission and by hydride-induced hydrogen stripping from the β-C. The products formed were the alkene, the aldehyde and hydrogen.

Falconer et al. [14] studied the decomposition of deuterated formic acid (DCOOH) on Ni on SiO_2 catalysts using TPD. CO_2, D_2, HD, HDO, H_2O and CO were the decomposition products of DCOOH. The results of this study are in agreement with single crystal studies. A bimolecular reaction mechanism was proposed: the acid hydrogen atoms were used in the formation of H_2O, while the carbon-bonded hydrogen mainly forms molecular hydrogen.

Fawcett et al. [15] describe a device that can do simultaneous XRD and DSC studies on a sample. One of the samples described in their article is malachite $(Cu_2CO_3(OH)_2)$, which decomposes into CuO, CO_2 and H_2O. CuO can be monitored by XRD and the gaseous product by mass spectrometry.

Temperature-programmed reaction spectroscopy

Temperature-programmed reaction spectroscopy is becoming increasingly attractive in studies of methanation, denitrification and desulphurization. Methanation is a TPRS technique and is omitted here because it has already been discussed in the section titled 'Methanation'.

Biermann et al. [16] used a Tian-Calvet heat-flow calorimeter to measure the heat of the reaction of NO, NH_3 and O_2 over a V_2O_5 on TiO_2/SiO_2 and a CuO on SiO_2 catalyst. The heat sensors of the DSC are placed around a quartz tube containing the catalyst. A dynamic calibration technique using a probe that operates on the basis of the Joule effect was developed to calibrate the system under flow conditions [16a]. For this system gas flows up to 200 cm^3 min^{-1} and grains around the probe showed no significant changes in the ratio of heat production and response.

It was suggested that the type of DSC used could be useful in screening catalysts for the selective catalytic reduction of NO with NH_3 in the presence of O_2.

Panayotov et al. [17] investigated the interaction between NO and CO on the surface of alumina-supported $CuCo_2O_2$-spinels at 293-703 K, using infrared and TPD methods. They concluded from the TPD spectra for adsorbed NO, CO and mixtures of NO and CO, that adsorption takes place entirely on the spinel. A $(CO.NO)_2^*$ complex was formed and the decomposition of the complex into N_2 and CO_2 was the rate-limiting step. It was suggested that oxygen from the catalyst surfaces competes with NO during the interaction with CO which results in a weakening of the metal-oxygen.

The preparation and characterization of high surface area $La_{1-x}Sr_xCoO_3$ (x = 0.3, 0.5, 0.6, 0.7) in relation to flue gas desulphurisation was reported by

Hibbert and Campbell [18]. TPD-MS and TGA of $La_{1-x}Sr_xCoO_3$ for exposure to sulphur dioxide and carbon monoxide were performed for the gases separately and for their mixtures. The catalyzed reaction of SO_2 and CO to give S_2 and CO_2 is suitable for the removal of sulphur dioxide from flue gases. A mixture of sulphates and sulphides was found after exposure to both gases, and the original structure of the catalyst was lost and replaced by a mixture of sulphides and oxosulphides of the metals. Comparison of TPD-MS and TGA showed that thermogravimetric analysis is not as sensitive to multiple desorption of species as is TPD-MS particularly at high rates of heating ($30\ K\ min^{-1}$).

Tin(II)chloride and zinc chloride were selected as the most effective catalysts for the hydropyrolysis of coal. The optimum catalyst load for both materials proved to be 10% resulting in conversion of about 85% of coal at 870 K, as reported by Sulimma et al. [19].

The characterization of the dispersion and state of Group VIII metals in unsupported CoMo-, FeMo- and NiMo-sulphide HDS catalysts were studied by Gobölös et al. [20] on the basis of TPD, TPS, TPO and TPR. In their study of these catalysts they found that the HDS activity of CoMo-sulphide catalyst is linearly dependent on the amount of NO adsorbed on the Co present in the CoMo-sulphide catalyst.

The ammonoxidation of 3-picoline to nicotinonitrile over a V_2O_5 catalyst was described by Andersson [21] using TPD accompanied by pulses of the reactants during the rise of temperature or at constant temperatures. Three different sites were available for the formation of the nitrile: chemisorbed 3-picoline and NH_3 adsorbed on the two remaining sites, one NH_3 molecule adsorbed on a vanadyl oxygen vacancy and the other in the form of a $-NH_2$ or $=NH$ group.

Zeolites

Zeolites have been of interest as catalysts because of the high activity and selectivity they show in a variety of acid-catalyzed type of reactions. Therefore, knowledge of the acid properties and the determination of the acid strength is important in catalyzed hydrocarbon reactions such as cracking.

Aboul-Gheit at al. [22] suggested a method using a DSC to determine physically and chemically adsorbed phases of presorbed triethyl amine. The heat evolved during temperature-programmed desorption is related to the amount of triethyl amine that desorbs from the site having acid strength. The DSC provides the quantitative information [22a]. The DSC technique described can be used to determine the acidity distribution of materials such as alumina and amorphous silica-alumina. However, zeolites whose water-desorption peaks cover a wide temperature range in the TPD spectrum and interfere with the triethyl amine desorption peaks appearing between 673 and 1073 K, cannot be investigated in this way. To overcome the problem of interfering peaks a so-called nullifying procedure was developed. The sample cell contained the amine adsorbed on zeolite, whereas the reference cell contained an equal amount of the amine-free zeolite.

A phosphorus-modified ZSM-5 zeolite was prepared by Jingfa et al. [23] for the production of diethyl ether from ethanol. The catalyst was characterized by techniques such as TPD, IR spectroscopy and XPS. TPD experiments of ammonia, ethanol and diethyl ether were performed at 393 K and room temperature respectively. Desorption was carried out in flowing hydrogen at a heating rate of 20 K min-1. The highest amount of ammonia was adsorbed by the catalyst containing phosphorus. This effect was ascribed to the ability of phosphorus to increase the acidity of the catalysts. Moreover, no carbonaceous residue was found on the working catalyst. The results indicate that the strongly acidic centres favour olefin formation, while the weakly acidic centres favour diethyl formation.

Auroux et al. [24] used a combined TG-DSC apparatus for the characterization of zeolites ZSM-5, H-Y and H-Ferrierite to determine the strength and number of acidic sites on different zeolites. The samples show a great heterogeneity in acid strengths. Three endothermic peaks were detected at 383 K. Averages of the total adsorption strengths, including the weak acid strength for these zeolites, were 155, 138 and 155 kJ.mol-1 respectively and this is very close to the values obtained by the static pulse method.

Bagnasco et al. [25] compared DSC and XRD in the study of the interaction of MgO and Al_2O_3 after addition of these materials to ZSM-5 zeolite. The presence of MgO and the formation of a magnesium spinel phase in the catalyst was more easily detected by means of DSC than through XRD.

Metal-support interaction

Hong and Yeh [26] used the temperature-programmed H_2 adsorption/desorption and volumetric techniques as indicators for the monitoring of electronic interactions between metal crystallites and support of Pd on titania catalysts. H_2 adsorption/desorption experiments were carried out on prereduced samples. Hydride formation was found at increasing hydrogen pressure under isothermal conditions and a lowering of desorption temperature on isobaric conditions. They interpreted the results as a transfer of electrons from the titania to Pd.

Differential thermal analysis and thermogravimetry were employed by Jinxinang et al. [27] in a study of the reduction-oxidation behaviour of unsupported and supported ruthenium components to characterize the extent of metal-support interaction, and the sintering stability of the ruthenium crystallites. The interaction between the ruthenium component and alumina was found to be stronger than that between the ruthenium component and silica. The sintering stability was studied on the basis of the DTA reduction procedure after repeated oxidations. It was found that the sintering stability of the respective 5% catalysts is inferior compared with the 1% Ru on SiO_2 or Al_2O_3 catalyst.

The reaction of vanadyl triisobutoxide with surface hydroxyls for the deposition of vanadium oxide species on various supports, such as TiO_2, Al_2O_3, SiO_2 and MgO, was reported by Kijenski et al. [28] . The oxidative and acidic properties of the catalysts were tested for methanol and n-

heptanol oxidation. It was found by means of TPR that the temperature of maximum hydrogen consumption depended on the support and increased in the sequence of TiO_2, Al_2O_3, SiO_2 and MgO. These results were consistent with the results of ESR measurements on the catalysts.

The molybdenum-support interaction of MoO_3 on SiO_2 and MoO_3 on Al_2O_3 were studied by Daly et al. [29] using nitric oxide chemisorption and TPD. The results suggested that the reactivity of Mo sites for disproportionation of chemisorbed NO to N_2O may be related to molydenum-support interaction.

Carbonaceous deposits

In many hydrocarbon reactions carbonaceous deposits (coke formation) may be formed on the surface of the catalysts. These deposits reduce the activity of the catalyst.

Coke on naphtha-reforming catalysts was characterized by TPO. TPO was used by Mieville [30] in conjunction with a microgravimetric reactor. Two different feeds, naphtha and n-heptane were used as sources for coke formation. With the naphtha feed coke formation was higher, the coke was predominantly formed on sites of alumina. Using n-heptane as a source of coke the Pt on alumina catalyst generated comparatively more coke with a higher proportion associated with Pt. The TPO results showed that platinum containing catalysts producing similar amounts of coke from naphtha have similar deactivation rates.

Al-Sammerrai et al. [31] reported a simple and rapid TGA/DTG method for the determination of deposited carbon on reforming catalysts. The catalyst was heated in nitrogen up to 1073 K, cooled and then heated in oxygen. The transition occurring between 723 and 873 K was attributed to the weight loss upon formation of carbon dioxide as a result of oxidation of the remaining deposited carbon. The method allows measurements of carbon amounts of about 0.01% (wt).

Hatcher and Burton [32] used a thermobalance to monitor the course of the oxidation reaction on a single catalyst pellet and, together with the analysis of effluent gas the determination of the rate of coke burning from fouled catalysts.

Studies of techniques

Leparlouer et al. [33,33a] introduced a TG-DSC system designed for a variety of experiments, such as physisorption at low temperature, chemisorption, heterogeneous catalysis, oxidation, reduction surface reactivity etc. This instrument (DSC) was used by Biermann et al. [16] and by Auroux et al. [24].

The concept of a mixing cell was employed by Huang and Schwartz [34] to describe mass transport during the nonisothermal operation of a TPD experiment. In such a model the number of mixing cells in a cascade of mixing cells is chosen in such a way that axial dispersion of gas phase species is described. It was concluded from the study by mathematical simulation of

thermal desorption from porous samples that in the absence of intraparticle diffusion the mass transfer effects on TPD require a nonsteady mass balance including both axial dispersion and convective transport.

Experiments using DSC for the determination of integral heats of adsorption of hydrogen on Pt dispersed on a variety of oxide supports showed values which were far too high. Sen et al. [35] ascribed this to changes in the thermal conductivity of the gas mixture H_2 and Ar in the sample cavity of the DSC, relative to the reference cavity. The errors introduced can be significantly reduced by using He as a carrier gas and by working at low H_2 pressures.

Miscellaneous studies

The effect of ageing in a water-containing atmosphere of Cu(II)O on activated carbon has been studied using DSC by Ehrburger et al. [36]. The DSC trace of the untreated sample shows three peaks, one attributed to H_2O desorption and two exothermal peaks attributed to the presence of CuO. DSC traces of aged (25 days) samples show an additional peak which could be ascribed to the crystallisation of CuO. After prolonged ageing times basic cupric carbonate was formed. The authors concluded from their experiments that the carbon support appeared to be the reducing agent of Cu(II) into Cu(I).

Takita et al. [37] found on the basis of TPD of water and oxygen that at least three kinds of adsorbed oxygen on Co_3O_4 samples were present and that these types desorbed at temperatures of about 350, 500 and >600 K. Preadsorption of water decreased the oxygen that desorbs at temperatures above 600 K, whereas the '350 and 500 K oxygen' were rearranged into an oxygen species which desorbs at a temperature of about 400 K.

The communication of Uhm and Lee [38] reports the surface modification of Pt on alumina and Pt on silica catalysts by various heat treatments. TPD of H_2 was used after each heat treatment. It was found that different heat treatments followed by rapid cooling with liquid nitrogen can generate more active sites that are located at the corner atom sites of the surface.

TPD has been used by Gillet et al. [39] to investigate binding states of CO on well-defined particles of Pd in the size range of 2-20 nm. Small particles (< 5 nm) produce higher CO binding states and during the desorption part of the adsorbed CO dissociates. These effects are ascribed to the high proportion of edge sites on smaller particles. The large values of the initial sticking coefficient on small particles were interpreted with a migration process of CO molecules on the silica substrate.

Roder et al. [40] studied the oxidation of CO on unsupported, supported and Pd-doped vanadia catalysts using a DSC coupled to a gas chromatograph. An O_2 pulse was introduced to unsupported V_2O_5 at temperatures in the range from 700 to 850 K. A reversible uptake and release of O_2 was observed. It was therefore suggested that vanadia is oxygen-deficient in an inert gas atmosphere. The initial oxygen deficit was attributed to the presence of V^{4+} ions at the surface. The amount of V^{4+} ions increases going

from 770 to 850 K. The results obtained after introducing pulses of CO/O_2 mixtures revealed that lattice oxygen is also involved in the oxidation of CO, even with gas phase oxygen in excess.

Leary et al. [41] considered the application of TPD and TPR for the study of subsurface diffusion in high surface area powders of Mo_2C. Two peaks were found in the TPR spectrum. The low temperature peak (479 K) was attributed to surface oxygen and the second peak to oxygen that had diffused into the subsurface region of the catalysts during the temperature ramp. For carbon-deficient catalysts only one TPR peak at 510 K is found. The effect of subsurface diffusion on TPD and TPR was described by a model which is able to explain the changes in the spectrum caused by varying the Mo/C ratio.

Ren-Yuan et al. [42] used Mössbauer spectroscopy with a modified sample holder which allows in situ TPR, TPD, TPO and TPSR. Two Fe on alumina catalysts with BET areas of 209 and 140 m^2 g^{-1} respectively were used. Hydrogen reduction of the high surface area catalyst occurred at three temperatures 733, 1063 and above 1123 K. In the first reduction stage the reduction of Fe(III) to Fe_3O_4 and then Fe_3O_4 to Fe(II) aluminate occurred. Fe_3O_4 was converted into Fe(II) and Fe(III) aluminates at temperatures in the range of 743-873K. In the range from 873 to 1123 K Fe(III) aluminate was reduced to Fe(II) and Fe(0).

Arnoldy et al. [43] compared temperature-programmed sulphiding (TPS) patterns with TPR patterns which were used to characterize CoO on Al_2O_3 catalysts. Sulphidation in H_2S/H_2 measured by means of TPS is much faster than reduction in H_2 measured by means of TPR. H_2S is thus the primary reactant in O-S exchange reactions whereas H_2 plays a minor role.

Bond and Sarsam [44] used TGA, DTA and TPR in their study of structural changes occurring during the calcination and subsequent reduction of precursors to Ni on MgO catalysts. Calcination of the catalysts for 4h at 773 K led to the diffusion of most of the Ni^{2+} ions into the MgO lattice. These ions were not reducible below 1073 K. The entry of the Ni^{2+} ions begins at defects or imperfections formed during the transformation of the hexagonal brucite to the cubic MgO as a cause of dehydration of $Mg(OH)_2$.

The objective of the study of Huang et al. [45] was to examine the changes in surface structure after hydrogen TPD and CO adsorption on Ni on alumina catalysts. A mechanism for metal-support interactions was proposed to account for the suppression of hydrogen chemisorption on nickel. XPS was used to examine the chemical changes during each experimental procedure.

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