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Catalytic transfer hydrogenation of 2-butanone on MgO. New active surface sites generated by treatment with chloroform

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In the course of heterogeneous catalytic transfer hydrogenation (CTH) of carbonyl compounds with alcohols on MgO, the catalyst is continuously poisoned, which leads to a complete loss of activity. The main result of the present work is that deactivation may be prevented by treatment with chloroform and the initial activity of MgO is retained for as long as 65 h. Detailed investigations were carried out (activations of MgO, TG, DSC, chloroform treatment, FT-IR spectroscopy, $CDCl_3$ adsorption) in order to identify both types of active centers responsible for poisoning and CTH. Based on our own experimental results as well as on data in the literature, the prerequisites of CTH on MgO appear to be basic (O^{2-}) site and adjacent surface hydroxyl site pairs. Lewis acid centers responsible for poisoning are blocked and active surface hydroxyl groups of weakly acidic character are simultaneously generated by chloroform treatment.

Keywords: catalytic transfer hydrogenation, 2-butanone, 2-propanol, chloroform, magnesium oxide, deactivation, FT-IR, surface poisoning species

1. Introduction

Catalytic transfer hydrogenation (henceforth abbreviated CTH) as a reduction procedure is widely used in preparative organic chemistry, employed both in the liquid and the vapour phase [1–3]. This procedure is applicable to all reducible functional groups using as catalysts metals, supported metals or metal oxides. Proving the applicability of the procedure, ketones are easily reduced by CTH using mostly oxides as catalysts and alcohols as hydrogen donors. According to the published results, MgO proved to be the most efficient oxide catalyst in the CTH of ketones in the vapour phase [4–7].

In spite of the many investigations [5–17], the mechanism of CTH of ketones is still unclear, the conclusions of various research groups being very different. In all the suggested mechanisms the key step is the transfer of a hydride anion from the carbon bearing the OH group to the carbonyl carbon, which has been proven using deuterium-labelled alcohols. The proposed mechanisms are, however, different regarding the way substrates are adsorbed and the nature of active sites.

In our previous work in this field [18], it was found that during vapour-phase CTH of ketones with 2-propanol the surface of MgO was poisoned. An efficient method was proposed to prevent deactivation, using treatment of the catalyst with carbon tetrachloride. Here we disclose our results obtained during CTH of 2-butanone on MgO treated with chloroform. In this case the deactivation of the catalyst was not observed even after 65 h of work. Based on the results of reactions carried out on differently activated catalysts, combined with the results of characterization of MgO and adsorption experiments monitored by FT-IR spectroscopy, a reaction mechanism is proposed for vapour-phase CTH of ketones on MgO.

2. Experimental

2.1. Materials

MgO was purchased from Fluka (Fluka 63091 MgO light, purum p.a.) and had a BET surface area of 64 $m^2\,g^{-1}$ determined with a Gemini 2375 V3.02 apparatus. The organic compounds used were Aldrich products of analytical grade and were purified by distillation prior to use. The purities of helium and oxygen used during this work were both 99.996%.

2.2. Methods

2.2.1. Catalytic transfer hydrogenation

CTH was studied in the vapour phase in a continuous-flow system. The apparatus has been described earlier [18]. Samples were withdrawn from the product flow leaving the reactor at regular intervals by means of an automated sampling valve and analyzed by an on-line SRI 8610A gas chromatograph equipped with a DB-WAX column (30 m, 0.53 mm I.D., 0.5 μm film thickness) and a flame ionization detector. Products were identified on the basis of their

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retention time and by GC-MS analysis (HP 5890 GC with a 50 m long HP-1 capillary column + HP 5970 MSD). In a typical experiment MgO was placed in the reactor and activated at 673 K by passing a mixture of helium and oxygen for 2 h (unless otherwise mentioned). The catalyst was then cooled to reaction temperature (523 K) in flowing helium and, finally, the gas was switched to the combined gas flow containing the reactant vapours. Treatment with chloroform was effected at 523 K in helium by injection of five pulses of 5 μl each, with 1 min time intervals between pulses. The system was then purged with helium for 15 min before the reaction was started. The treatment during the reaction was carried out by injecting chloroform pulses into the feed.

2.2.2. Characterization of the catalyst

The chlorine content of the catalyst after treatment with chloroform was determined by titration according to the Volhart method. X-ray diffraction measurements were taken on a Philips PW 1710 BASED diffractometer using Cu Kα radiation. Thermal analysis was carried out with a Derivatograph-Q (MOM, Budapest, Hungary) and differential scanning calorimetry measurements were performed in a Perkin–Elmer DSC-2 equipment.

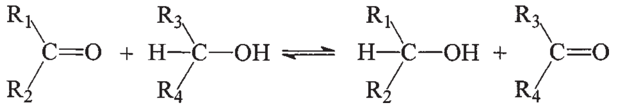
For adsorption measurements all adsorbates were degassed *in situ* with the freeze–pump–thaw technique prior to the adsorption runs. For the infrared spectroscopy (FT-IR) study self-supporting thin wafers (30 mg with 10 mm diameter) of the catalyst were placed in a conventional vacuum system equipped with an IR cell. The sample was activated at 673 K for 2 h at a residual pressure of ca. 10^{-3} Torr and cooled to the temperature of the adsorption experiments, 523 K. After a 15 min exposure to the vapours of the organic compounds, the sample was degassed for 10 min and cooled to room temperature for recording the spectra using a Mattson Genesis 1 FT-IR spectrometer with a 2 cm^{-1} resolution. Spectra of adsorbed species were obtained by subtraction of the catalyst spectra.

The reaction of chloroform on MgO was studied also by the pulse method [19]. The catalyst was placed in a glass microreactor, activated as previously described, cooled to 523 K in helium flow and ten pulses, 0.3 μl each of chloroform were injected into the gas flow by a gas-tight microsyringe. The products were analyzed by a GCHF 18.3 gas chromatograph equipped with a packed column (20% β,β'-oxydipropionitrile/Chromosorb W, 2 m, 4 mm I.D.) and thermal conductivity detector. The products were analyzed by GC-MS (see above).

3. Results and discussion

3.1. Catalytic transfer hydrogenations

CTH of ketones using alcohols as hydrogen donors takes place according to scheme 1. During the reaction 2-propanol is reduced to acetone. Dehydration of 2-propanol could also occur. In the experimental conditions used in this study the formation of propene was negligible and occured only at early stages of the reaction. Treatment with chlorinated hydrocarbons has been widely applied in heterogeneous catalysis in order to increase selectivity [13,20,21]. Kaspar et al. [6] studied CTH of 4-hexen-3-one on MgO and reported the effect of Cl$^-$ ions on product selectivity. The basicity and the morphology of the catalyst were altered and, consequently, side reactions were minimized.



Scheme 1. Reaction scheme of CTH of ketones using alcohols as hydrogen donors.

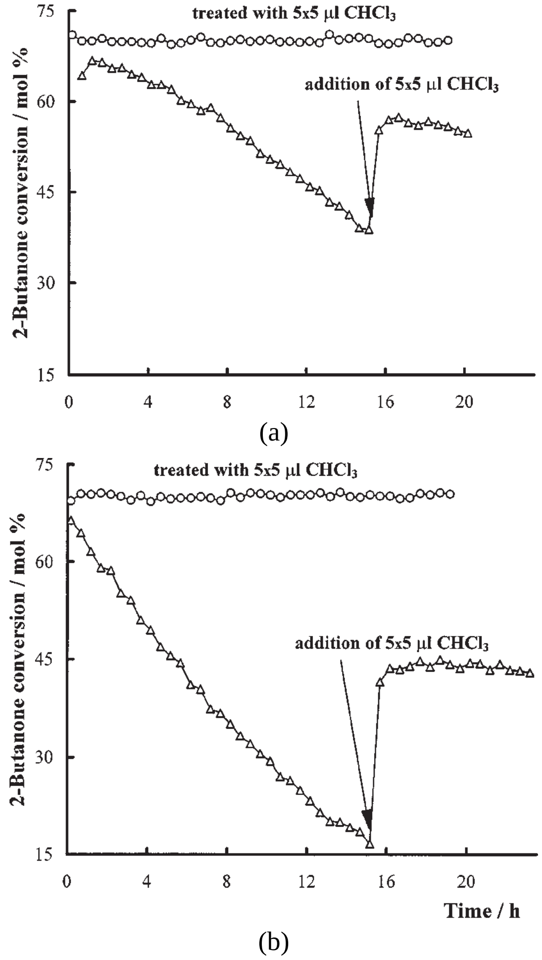
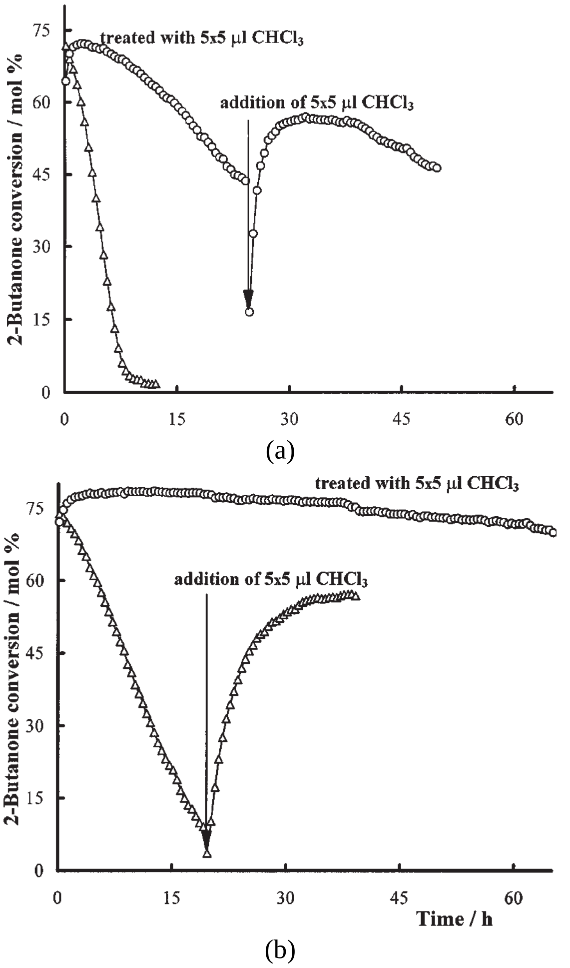


Figure 1. CTH of 2-butanone with 2-propanol over 8 mg MgO. Activation in 40 cm^3 min^{-1} He–O$_2$ (1 : 1) at (a) 573 and (b) 673 K; reaction conditions: 20 cm^3 min^{-1} He at 523 K, HLSV 0.75 cm^3 g^{-1} h^{-1}, 2-propanol/2-butanone molar ratio 2.5; treatment with chloroform at 523 K.

The effectivity of chloroform treatment preventing MgO poisoning during CTH of 2-butanone was studied in reactions run for one or several days using different activation conditions. The results obtained are presented in figures 1 and 2. No condensation products of ketones were detected in the gas phase, the selectivity of the reduction to 2-butanol



(a)

(b)

Figure 2. CTH of 2-butanone with 2-propanol over 8 mg MgO. Activation in (a) 20 $cm^3\,min^{-1}$ He and (b) 60 $cm^3\,min^{-1}$ He–O_2 (1 : 1), at 673 K; reaction conditions: 20 $cm^3\,min^{-1}$ He at 523 K, HLSV 1.00 $cm^3\,g^{-1}\,h^{-1}$, 2-propanol/2-butanone molar ratio 3.5; treatment with chloroform at 523 K.

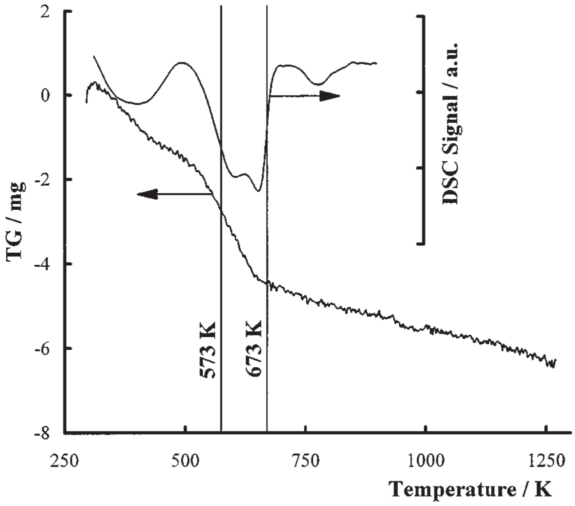


Figure 3. TG and DSC curves of MgO. TG measurement: 96.55 mg sample, dry air stream, heating rate 10 $K\,min^{-1}$; DSC analysis: 9.6 mg sample, N_2 stream, heating rate 20 $K\,min^{-1}$.

exceeded 98% in each case. The by-products formed were olefins (2-butenes and 1-butene) and after 1–2 h use of the catalyst the 2-butanol selectivity became near 100%.

The surface of the catalyst not treated with chloroform was rapidly poisoned (figure 1). MgO activated at 573 K was poisoned considerably more slowly than that activated at 673 K. At the same time it is shown by the TG and DSC curves (figure 3) that dehydration of the surface is not yet complete at 573 K. The sharp decline corresponding to dehydration on the TG curve is below 673 K and it is at approximatively this temperature that the corresponding endothermic peak of the DSC curve reaches the baseline. Accordingly, the surface of the catalyst activated at 573 K is still partially covered by residual OH groups.

In both cases, the surface of the poisoned catalyst is partially regenerated by a treatment after 15.3 h on-stream with five pulses of chloroform. After the treatment, the conversion of 2-butanone sharply increased. In the case of the catalyst activated at 573 K this came closer to the initial conversion value, then remained constant within the time period studied. In contrast, the catalyst treated with chloroform prior to the reaction does not lose any of its activity even after 19 h on-stream, after activation at either temperature. The effect of chloroform administered in the course of the reaction allows us to conclude that the decrease in catalyst activity was brought about by the formation of two different types of surface species. One of these is irreversibly bound and may not be removed, while the other may be displaced from the surface by chloroform treatment applied during the reaction.

When the composition and flow rate of the gas mixture used for activation were varied (figure 2), the decrease in conversion was much faster in the case of MgO activated in 20 $cm^3\,min^{-1}$ He than of the catalyst activated in 60 $cm^3\,min^{-1}$ of a 1 : 2 mixture of He and O_2, in spite of the fact that the higher flow rate applied during activation increases the rate of dehydration, and – as established above – a more extensive dehydration leads to a faster poisoning of the surface. The latter catalyst was gradually regenerated by chloroform treatment applied after 18.8 h. Conversion was stabilized at a value lower than the initial one (determined after 10 min) and remained constant for as long as 39 h on-stream. The decrease in activity seen immediately after the addition of chloroform could be due to the blockage of the oxygen sites of MgO by formation of surface hypochlorite species on the catalyst. These species are quickly decomposed at the reaction temperature, thus they may be present only after direct addition of the modifying agent. Conversion decreased even if the catalyst activated in 20 $cm^3\,min^{-1}$ He was treated with chloroform prior to the reaction. This could be explained by the generation of surface defects which could lead to a decrease of the number of basic sites. In contrast, if the catalyst activated in 60 $cm^3\,min^{-1}$ He–O_2 (1 : 2) was previously treated with chloroform, the conversion slightly increased and remained nearly constant even after 65 h on-stream. As one can see the effectivity of treatment with chloroform is highly dependent on the activation conditions of MgO. Considering

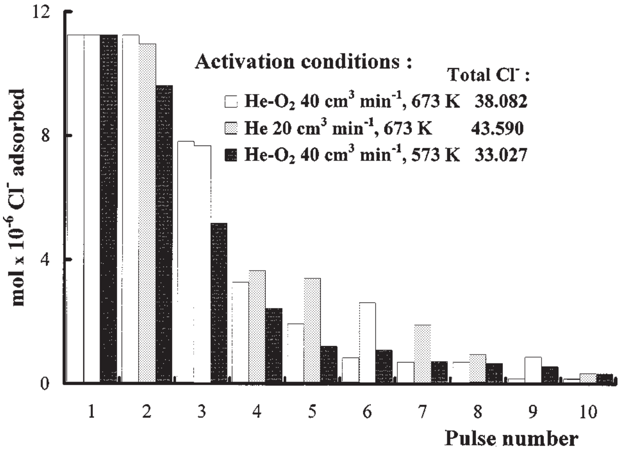


Figure 4. Reaction of chloroform on MgO. Reaction conditions: 20 $cm^3\,min^{-1}$ He, 523 K, 0.3 μl chloroform.

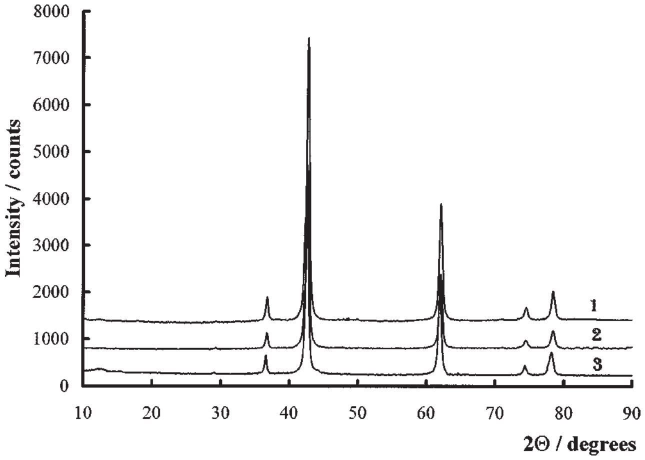


Figure 5. XRD patterns of MgO: (**1**) parent MgO; (**2**) MgO activated in 40 $cm^3\,min^{-1}$ He–O_2 (1 : 1) at 673 K 2 h; (**3**) MgO activated in 40 $cm^3\,min^{-1}$ He–O_2 (1 : 1) at 673 K 2 h, treated with chloroform 0.5 $cm^3\,g^{-1}\,h^{-1}$ at 523 K 1 h.

the results published so far on CTH of aliphatic ketones on MgO which demonstrated the necessity of surface basic sites [7,12,16], the results presented above suggest that the active site of the reaction includes a surface OH center, also. These centers function as weak Brønsted acid sites during the reaction.

3.2. Adsorption experiments

Since the effect of treatment with chloroform proved to be highly dependent on the MgO activation conditions, the reaction of chloroform on differently activated MgO was studied in a pulse system (figure 4). It was shown by GC-MS that, beside the unreacted chloroform, the resulting product is a mixture consisting mostly CO and a small amount of CO_2. Chlorinated products other than chloroform were not detected. MgO activated at 573 K binds 13% less Cl^- than that activated at 673 K and this significant difference manifests itself starting from the second pulse. Since chloroform is decomposed on Mg^{2+} and O^{2-} centers, the dehydration degree of the surface will influence the amount of Cl^- absorbed; however, even a smaller amount of bound Cl^- is able to completely prevent poisoning of MgO during CTH. It is therefore probable that the species poisoning the surface are formed on Lewis acidic centers and they also block part of the basic centers playing an essential role in the gas-phase CTH of ketones. The amount of Cl^- ions bound by the catalyst activated in helium is more than 14% higher than that bonded on the one activated in 40 $cm^3\,min^{-1}$ He–O_2 (1 : 1). This may be explained by an increase in the number of Lewis acidic centers. The significant difference was detected in pulses 4–8, which may indicate that new centers, energetically differing from the original ones, binding Cl^- at a lower rate are produced on the surface of MgO pretreated in He. In this case the role of surface defects generated is probably essential, since formation of such defects brings about a decrease in the number of surface O^{2-} centers.

As shown by the XRD data in figure 5, there is no significant difference between the diffractograms of the sample activated at 673 K before and after a prolonged exposure to chloroform. The chloride ion content of sample (**3**) was 1.1%, but no $MgCl_2$ phase appeared. No peaks other than those of cubic MgO (periclase) were detected in these diffractograms, which indicates that as a result of chloroform treatment the Cl^- was bonded only on the catalyst surface and no new detectable crystalline phase appeared.

Adsorption of the reactants, chloroform and chloroform-*d*, on MgO was studied by IR spectroscopy (figures 6–8). The IR spectrum of MgO activated at 673 K (not shown) displays a small, sharp adsorption band at 3745 cm^{-1} attributed to isolated OH groups on kinks or edges [22,23] and a broad band at 1400–1500 cm^{-1} with a shoulder at about 1600 cm^{-1}, which indicates the presence of residual surface carbonate. When MgO was activated at 573 K, the band at 3745 cm^{-1} was accompanied by a broad band at 3725 cm^{-1} associated with OH groups on the crystal faces interacting via hydrogen bonding.

The bands which appeared after adsorption of 2-propanol (figure 6(**1**)) indicated dissociative adsorption of the alcohol but undissociated alcohol species were also present on the surface. After adsorption of a mixture of 2-propanol and 2-butanone (figure 6(**2**)) the bands which appeared in the ν(CH) and ν(CO) region showed the adsorption of carbonyl compounds also. Two bands were detected in the ν(OH) region at 3725 and 3575 cm^{-1}, the latter being much more intense than the band which appeared after adsorption of 2-propanol. The sharp, intense band appearing at 1580 cm^{-1} was attributed to carbonyl species strongly bound to the surface of MgO [22]. As a result of adsorption of chloroform (figure 6(**3a**)) or chloroform-*d* (figure 6(**3b**)) on such samples the carbonyl band at 1580 cm^{-1} decreased significantly. Repeated adsorption of 2-propanol and 2-butanone mixture on these samples (figure 6 (**4a**) and (**4b**)) led to appearance in this region of a sharp, intense band at 1707 cm^{-1}. This band was attributed to loosely bound surface carbonyl species [22] or to H-bonded ketone, if the adsorption of ketone was preceded by alcohol adsorp-

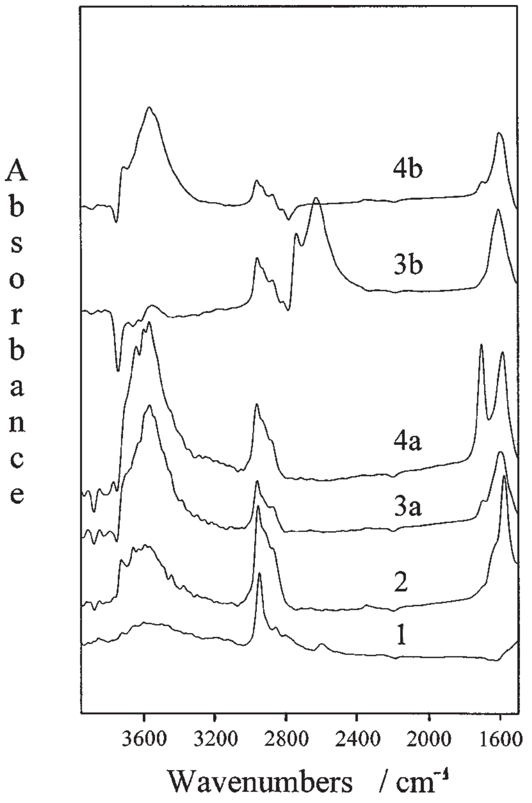


Figure 6. FT-IR spectra of species formed on MgO activated at 673 K for 2 h at a residual pressure of ca. 10^{-3} Torr and after treatment at 523 K with 20 Torr of 2-propanol (**1**); treatment with 40 Torr of 2-propanol/2-butanone = 1/1 mixture (**2**), followed by treatment with 35 Torr chloroform (**3a**), followed by treatment with 40 Torr of 2-propanol/2-butanone = 1/1 mixture (**4a**); or followed by treatment with 35 Torr chloroform-*d* (**3b**), followed by treatment with 40 Torr of 2-propanol/2-butanone = 1/1 mixture (**4b**).

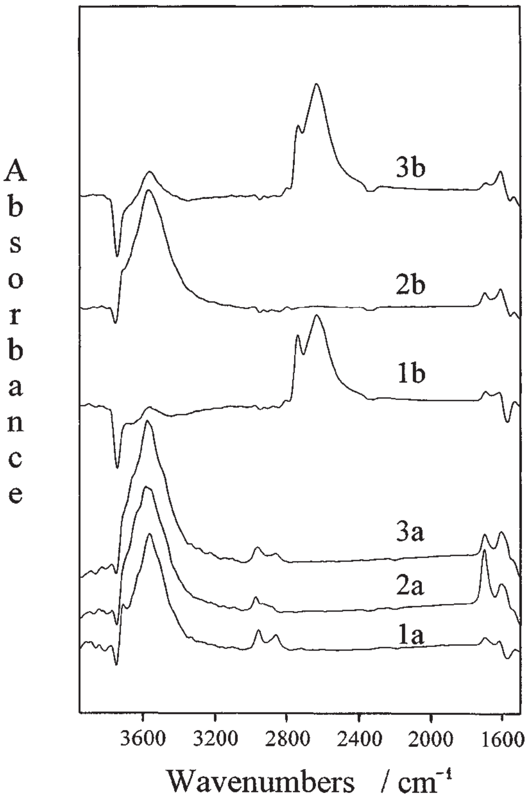


Figure 7. FT-IR spectra of species formed on MgO (conditions see figure 6) after treatment with 35 Torr chloroform (**1a**), followed by treatment with 40 Torr of 2-propanol/2-butanone = 1/1 mixture (**2a**); followed by treatment with 35 Torr chloroform (**3a**); and 673 K after treatment with 35 Torr chloroform-*d* (**1b**), followed by treatment with 40 Torr of 2-propanol/2-butanone = 1/1 mixture (**2b**), followed by treatment with 35 Torr chloroform-*d* (**3b**).

tion [13]. The intensity of this band was considerably lower in the case of the sample treated with $CDCl_3$ than in the case of the one treated with $CHCl_3$. We consider that this was due to an isotope effect, which indicates the participation of surface OH(D) groups in the adsorption of the ketone. If the adsorption of the mixture was carried out on samples firstly treated with chloroform or chloroform-*d*, the band at 1580 cm^{-1} had a very low intensity and the sharp, intense band at 1707 cm^{-1} appeared (figure 6 (**2a**) and (**2b**)). Further treatment of these samples with chloroform or chloroform-*d* lowered the intensity of these bands (figure 7 (**3a**) and (**3b**)). The same observation could be made on the sample activated at 573 K (figure 8).

According to the position of these carbonyl bands we suggest the formation of the surface species presented in scheme 2. We consider species **A** as species irreversibly bound to the surface of which the carbonyl band appeared at 1580 cm^{-1}. The formation of these species can be explained by the enhanced acidic character of the α-H which can interact with the strong basic sites of the surface leading to strongly bonded species. The carbonyl bands of species **B** also appeared around 1580 cm^{-1}, but these could be removed by treatment with chloroform during the reaction. Species **C** are weakly bonded to the surface; their carbonyl

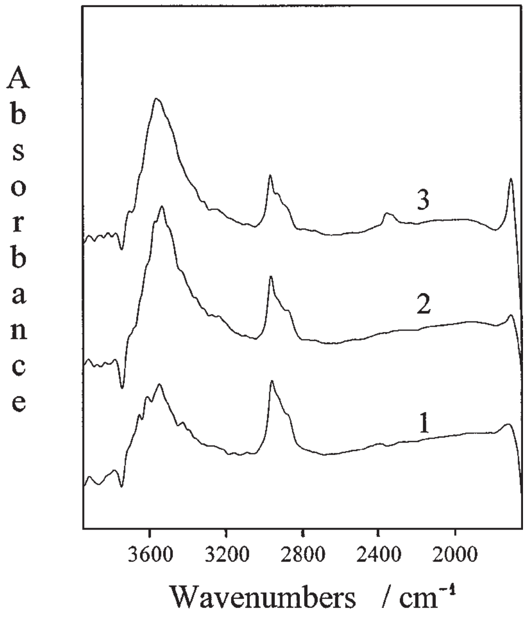
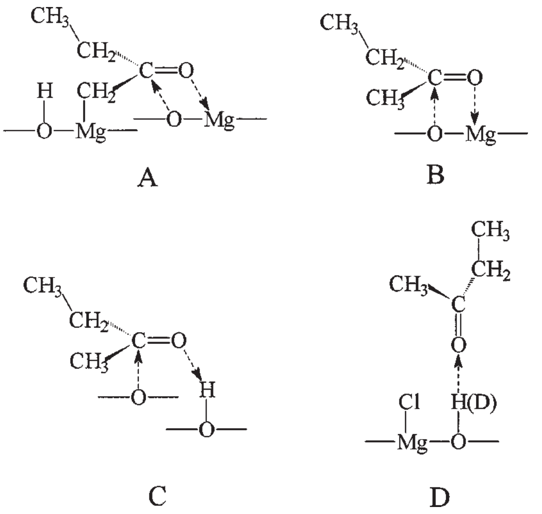


Figure 8. FT-IR spectra of species formed on MgO activated at 573 K (conditions see figure 6) after treatment with 40 Torr of 2-propanol/2-butanone = 1/1 mixture (**1**), followed by treatment with 35 Torr chloroform (**2**), followed by treatment with 40 Torr of 2-propanol/2-butanone = 1/1 mixture (**3**).

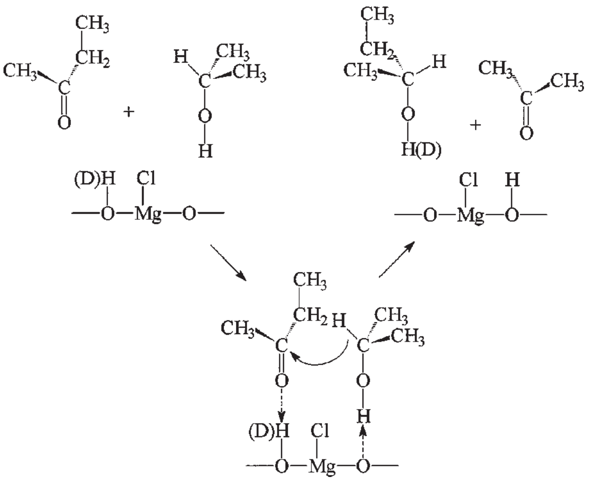


Scheme 2. Surface species formed during the CTH of ketones.

vibration band appeared at 1707 cm^{-1} and did not poison the catalyst. Species **D** are the species through which the reaction proceeds on a partially hydrated surface and which are removed from the surface by evacuation. The Cl^- impeded the adsorption of the ketones by covering the surface Mg^{2+} and prevented the formation of species **A** and **B** on these sites.

These assumptions were strongly supported by the bands appearing in the ν(OH) or ν(OD) region of the IR spectra. Adsorption of chloroform on the sample treated previously with the 2-propanol and 2-butanone mixture led to an increase in the OH band positioned at 3575 cm^{-1} and to further shift of the maxima towards lower wavenumbers (3565 and shoulder at 3535 cm^{-1}) (figure 6(**3a**)). If chloroform-*d* was adsorbed on the sample the OH bands disappeared almost completely and the corresponding OD bands appeared (2748 and 2643 cm^{-1}) (figure 6(**3b**)). Further treatment of these samples with 2-propanol and 2-butanone mixture resulted in shifting back the maxima of the OH band from 3565 to 3572 cm^{-1} and a decrease in the shoulder from 3535 cm^{-1} (figure 6(**4a**)), or in disappearance of the OD bands and reappearance of the bands in the OH region (figure 6(**4b**)). This indicated without any doubt the participation of the surface OH groups in the reaction, acting as active sites on which the ketone was adsorbed. The decrease of the band at lower wavenumbers, so corresponding to OH groups of more pronounced Brønsted acidic character, showed that these participate preferentially in the reaction. The same observations could be made in the case of the sample activated at 573 K (figure 8) and of the one treated firstly with chloroform or chloroform-*d* (figure 7).

The effect of Lewis acid sites as responsible for the strong adsorption of the ketones and, consequently, deactivation of the catalyst, was supported also by the very low intensity or even total absence of bands in the ν(CH) region of the spectra obtained after adsorption of the reaction mixture on samples previously treated with chloroform or chloroform-*d* (figure 7).



Scheme 3. Reaction path in CTH of ketones on MgO treated with chloroform.

As a result gas-phase CTH of ketones on MgO requires the presence of basic centers and adjacent weakly acidic OH groups, as shown in scheme 3. It was demonstrated that Lewis acid sites are responsible for catalyst deactivation during a prolonged exposure of the catalyst to the reaction mixture. The poisonous species are formed on Lewis acid–Lewis base site pairs by strong adsorption of the ketones present in the system. The beneficial effect of treatment with chloroform can be explained by covering the surface Lewis acid sites with Cl^- and the generation of active surface OH groups.

4. Conclusions

Gas-phase CTH of 2-butanone by 2-propanol was studied on MgO. It was established that catalyst activity decreases in the course of the reaction. The presence of surface OH groups retarded surface poisoning. Poisoning may be completely prevented by chloroform treatment following an appropriate activation of the catalyst, which then retained its initial activity for an extended time (65 h). The experimental results allowed the delineation of the probable structure of both surface species formed during CTH and the species responsible for catalyst poisoning. Chloroform treatment blocked Lewis acid centers which played a significant role in catalyst poisoning and simultaneously generated OH centers necessary for CTH. The active centers of CTH on MgO are composed of a basic site (O^{2-}) and surface OH site pair.

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