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Hydrogenation of unsaturated ketones: selective catalytic transfer hydrogenation of 5-hexen-2-one over MgO

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Abstract

In the present study the selective catalytic transfer hydrogenation of an unsaturated ketone is described. During the heterogeneous catalytic transfer hydrogenation of 5-hexen-2-one with 2-propanol to 5-hexen-2-ol on MgO, the catalyst was continuously poisoned, which lead to a complete loss of activity. The major point of the present work is that the deactivation can be prevented by treatment with chloromethanes. The best results were obtained on MgO previously treated with chloroform. As a result the selectivity of the formation of 5-hexen-2-ol was close to 100% and no catalyst deactivation was observed during the time period studied. Detailed investigations were carried out (MgO treatment with different organochlorine reagents, FT-IR spectroscopy, $CDCl_3$ adsorption, reaction of chloromethanes with MgO in pulse system) in order to optimize the reaction conditions and to certify the mechanism proposed earlier.

Keywords: Catalytic transfer hydrogenation; 5-hexen-2-one; 2-propanol; Chloromethanes; Magnesium oxide; Deactivation; FT-IR; Chloroform-*d*

1. Introduction

Hydrogenation of carbonyl compounds is one of the most active research areas in organic synthesis due to the great practical importance of the products [1]. The selective hydrogenation of unsaturated carbonyl compounds to the corresponding unsaturated alcohols is the focus of special interest since this is often a key step in the preparation of various fine chemicals. Excellent results have been obtained in the hydrogenation of unsaturated aldehydes using supported metal catalysts promoted with metal ions or bimetallic catalyst. However, these catalysts were proved to be inefficient for reduction of unsaturated ketones to unsaturated alcohols [1]. The catalytic hydrogenation of the unsaturated ketones mostly results in the selective hydrogenation of the C=C bond. This was demonstrated by the earlier experimental data [1], in agreement with more recent results [2–6]. The preparation of the unsaturated alcohols from unsaturated ketones became possible with good results by homogeneous catalytic hydrogena-

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tions [7–10]. Due to the well known advantages of the heterogeneous catalytic procedures this field still belongs to the frequently studied areas. The heterogeneous catalytic transfer hydrogenation (henceforth abbreviated as CTH) was found to be a possibly useful method for the synthesis of unsaturated alcohols [11].

Both the liquid and vapour phase CTH is a widely used procedure in organic chemistry due to the cheep catalysts and hydrogen donors used [11–13]. The method was found to be effective for the vapour phase reduction of ketones over MgO catalyst and using alcohols as hydrogen donors [14–16].

In our previous works we found that during vapour phase CTH of ketones with 2-propanol the surface of MgO poisoned, and we proposed efficient methods to prevent deactivation, namely treatments with carbon tetrachloride [15] or chloroform [16]. In the present paper we extended our studies in CTH and applied the earlier findings in the hydrogenation of 5-hexen-2-one.

As described, 5-hexen-2-one can be hydrogenated selectively to saturated ketone [2], and saturated alcohol [2,17] or to unsaturated alcohol in homogeneous systems [8]. However, the reduction to unsaturated alcohols in heterogeneous systems proved to be non-selective [18,19]. The results disclosed in this work will provide an effective, selective and convenient method for the reduction of 5-hexen-2-one to 5-hexen-2-ol. Although the catalyst was deactivated during the reaction, previous treatment with chloromethanes prevented the deactivation of MgO. At the same time these results gave new evidences to support our mechanistic explanation suggested earlier [15,16].

2. Experimental

2.1. Materials

MgO was a Fluka product (Fluka 63091 MgO light, purum p.a., $>98.0\%$) with a specific surface area of 64 $m^2\ g^{-1}$ (BET measurements were performed in a Gemini 2375 V3.02 apparatus). The organic compounds used were Aldrich products of analytical grade ($>98\%$) and were purified by distillation prior to use. Helium and oxygen used were Linde products with minimum purity of 99.996%.

2.2. Methods

2.2.1. Catalytic transfer hydrogenation (CTH)

CTH was carried out in the vapour phase in continuous flow system. The catalyst was placed in an 8 mm wide (i.d.) glass microreactor. Helium used as carrier gas was saturated with the vapours of the two reactants in separate saturators. The composition of the feed was controlled by changing the temperatures of the saturators and the velocities of the gases with maintenance of the total gas flow to a constant value. The two gas flows were unified and driven on the catalyst bed. Samples were withdrawn from the product flow after the reactor in every 30 min by an automated sampling valve. The analysis were performed by an on-line attached 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 the comparison of their retention time to authentic samples, and by GC-MS analysis (HP 5890 GC with 50 m HP-1 capillary column coupled with an HP 5970 MSD, E.I. 70 eV) of the product mixture. The values of hourly liquid space velocity (denoted as HLSV) were calculated from data published in the literature [20,21] and determined. The results were in good agreement.

In a typical experiment 21 mg of MgO was placed into the reactor and activated at 673 K in 40 $cm^3\ min^{-1}$ 1:1 mixture of He and O_2 gas flow for 2 h. The catalyst was then cooled to 523 K in 20 $cm^3\ min^{-1}$ flowing He and finally the reactant feed in He was driven into the reactor. The treatment of the catalyst with organochlorine reagents was carried out at 523 K in He. Five pulses, 5 μl each, of the

organochlorine reagent were injected, then the system was purged with He for 15 min before the reaction.

2.2.2. Adsorption experiments

For adsorption all adsorbates were degassed in situ with the freeze–evacuate–thaw technique prior to the adsorption studies. In the infrared spectroscopic (FT-IR) study self-supporting 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 pressure of ca. 10^{-3} Torr and then cooled to the temperature of the adsorption experiments, 523 K. After 15 min exposure to the organic compounds, the sample was evacuated for 10 min and cooled to room temperature. The spectra were recorded with a Mattson Genesis1 FT-IR spectrometer with a 2 cm^{-1} resolution. Spectra of the adsorbed species were obtained by subtraction.

The reactions of dichloromethane, chloroform and carbon tetrachloride on MgO was also studied by the pulse method [22]. In these experiments the catalyst was placed in a similar glass microreactor, activated as described above, cooled to 523 K in helium flow and 10 pulses, 1 μl each (unless otherwise indicated) of chloromethane were injected into the gas flow by a gastight microsyringe. The products were analyzed by a GCHF 18.3 (Berlin) 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 also analyzed by GC-MS (see above).

3. Results and discussion

3.1. Catalytic transfer hydrogenation

Our previous results [15,16] showed that MgO is poisoned during CTH of 2-butanone by 2-propanol. The optimal activation and reaction conditions were determined. During these experiments, in accordance with the literature [23], we pointed out that in the case of methyl alkyl ketones the increasing alkyl chain did not show a significant effect on catalyst poisoning. In the present work we extended our studies to an unsaturated ketone, 5-hexen-2-one. The results will be compared with those obtained using as substrate the corresponding saturated ketone, 2-hexanone. In Fig. 1a and b were plotted the conversions and C=O hydrogenation selectivi-

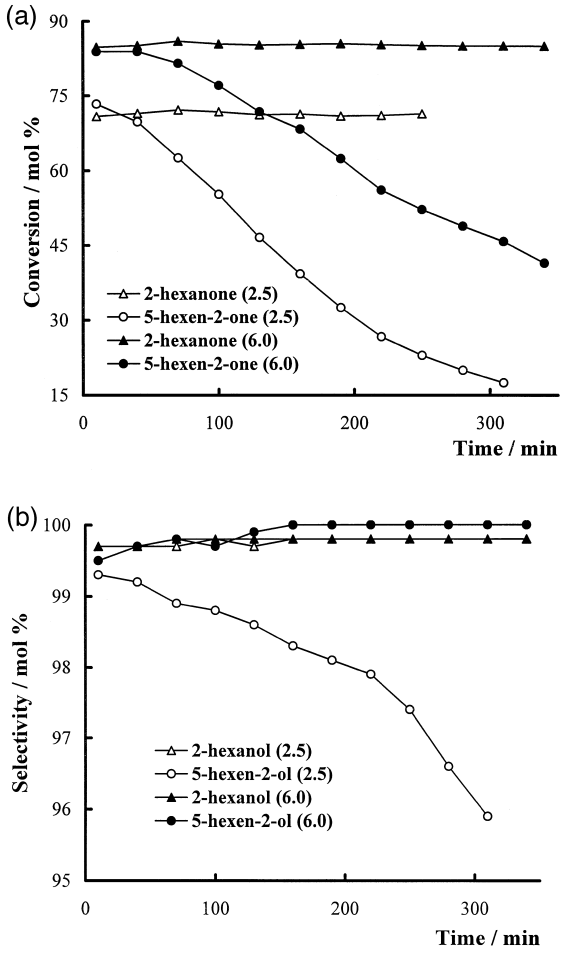

Fig. 1. (a) Conversion in CTH of 5-hexen-2-one and 2-hexanone with 2-propanol versus time on stream (21 mg MgO activated in 40 cm^3 min^{-1} $He–O_2$ 1:1 at 673 K, reaction conditions: 20 cm^3 min^{-1} He at 523 K, HLSV 0.16 cm^3 g^{-1} h^{-1}, 2-propanol/2-ketone molar ratio in parenthesis). (b) Hydrogenation selectivity in CTH of 5-hexen-2-one and 2-hexanone with 2-propanol versus time on stream (activation and reaction conditions see Fig. 1a).

ties as a function of time-on-stream using two different 2-propanol/ketone molar ratios.

As one can see from Fig. 1a and b, during the initial period the conversions of the two ketones are identical in the applied experimental conditions, however, as a result of the effect of the unsaturation in the alkyl chain MgO is rapidly poisoned. The selectivity of the hydrogenation of the C=O group is high in each case. By-products, especially 2-hexanone and 2-hexanol could be detected in the case of the unsaturated ketone at low reactant molar ratio.

The presence of the isolated C=C group led to a faster poisoning of MgO, due to the adsorption by the alkenyl chain anchoring on the surface. According to the literature the metal ions interact with the π-bond and the oxide ion may attract the H from the allylic position leading to a much stronger adsorption of the substrate [24,25]. This surface intermediate can form polymerized products on the surface, which will cover irreversibly and deactivate the MgO. This stongly supports that Lewis acid sites have a crucial role in catalyst poisoning. In this case these sites are responsible for the strong adsorption of the C=O [16] and the C=C group, respectively.

In order to prevent deactivation during the reaction of saturated ketones we proposed treatment of MgO with carbon tetrachloride [15] or with chloroform [16] prior to the reaction. Both methods were found to be effective in preventing the deactivation of the catalyst, which in case of treatment with chloroform kept its initial activity for more than 65 h. The results obtained after treatment of MgO with organochlorine reagents in the case of 5-hexen-2-one are shown in Fig. 2a and b.

Fig. 2a shows that treatment with chloroform was found to be the most effective to avoid MgO poisoning. In this case the conversion of 5-hexen-2-one remained constant during the whole period of time studied. In the case of treatment with dichloromethane or carbon tetrachloride after 300 and 200 min long reactions, respectively, the catalyst started to loose its

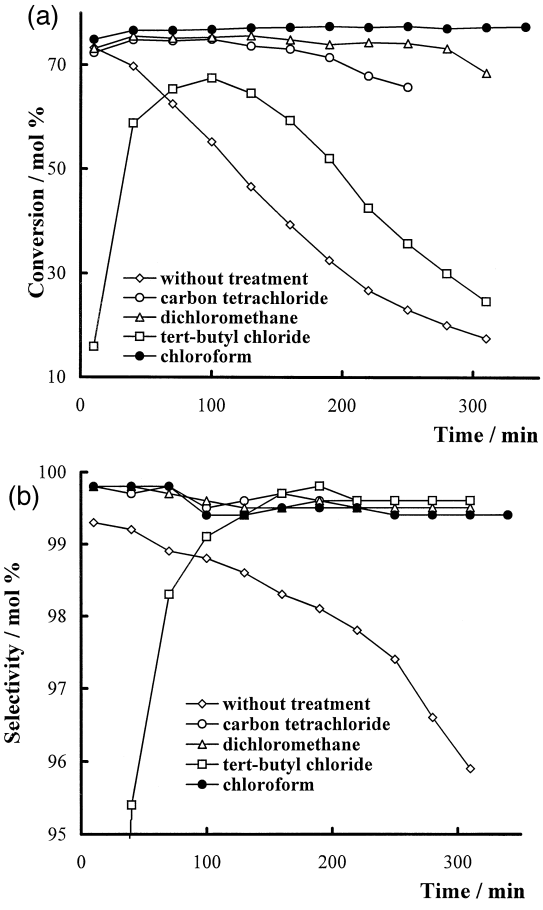

Fig. 2. (a) 5-Hexen-2-one conversion in CTH with 2-propanol on MgO treated with organochlorine reagents versus time on stream (activation and reaction conditions see Fig. 1a, treatment in 20 cm^3 min^{-1} He at 523 K with 5×5 μl pulses of the organochlorine reagent). (b) 5-Hexen-2-ol selectivity in CTH of 5-hexen-2-one with 2-propanol on MgO treated with organochlorine reagents versus time on stream (activation and reaction conditions see Fig. 1a, treatment conditions see Fig. 2a).

original activity. The effect of *tert*-butyl chloride was not satisfactory: the conversion after 80 min was sligthly higher than in the case of the non-treated MgO. During the initial period the conversion of 5-hexen-2-one was much smaller. This can be the result of the steric hindrance of *tert*-butyl cations formed by decomposition of *tert*-butyl chloride which are weakly adsorbed on the basic centers of the catalyst. They, however, are easily removed by the reactants during the reaction which was confirmed by the presence of isobutylene in the

product mixture. In addition, *tert*-butyl cations adsorbed on basic sites may also cause lower selectivities of 5-hexen-2-ol during the initial period (Fig. 2b). This low selectivity provides a new evidence for proving that CTH of ketones on MgO proceeds on sites which include a basic surface center. If these centers were partially occupied by *tert*-butyl cations like in our case in the early stages of the reaction, the concurrent dehydration of the formed alcohol on acidic sites not covered by Cl^- can occur. After 100 min of reaction the selectivity of the unsaturated alcohol reached values higher than 99.5% similarly to the selectivities obtained on MgO treated with other organochlorine reagents. No isobutylene was detected in the product mixture.

Treatment with chlorinated hydrocarbons has been widely applied in heterogeneous catalysis in order to increase selectivity. Observations concerning the modifying effect of Cl^- ions on MgO have also been published. Burch et al. [26,27] and Sugiyama et al. [28,29] investigated the effect of CH_2Cl_2 and CCl_4 on the activity and selectivity of oxidative coupling of methane on MgO. The selectivity of ethylene formation was increased by the introduction of chlorinated compounds. Kaspar et al. [30] studied the CTH of 4-hexen-3-one and reported the advantageous effect of Cl^- ions on product selectivity. The basicity and the morphology of the catalyst were altered and, consequently, side reactions were minimized.

The results described above proved that treatment with chloroform effectively prevents poisoning of MgO during CTH of unsaturated ketones, too. Based on previously published experimental results [15,16] we reached to the conclusion that in the case of saturated ketones the surface species responsible for poisoning are formed on Lewis acid and Lewis basic site pairs. The active sites in CTH of ketones are formed from a basic center and a slightly acidic center which may be a surface OH group. The effect of treatment with chloromethanes in CTH of ketones was explained by the responsibility of the Lewis acid sites for catalyst poisoning. These sites were covered by Cl^-, and new active OH groups were generated on the surface [16]. These earlier conclusions were confirmed by the results presented above, obtained using as substrate 5-hexen-2-one.

3.2. Adsorption studies

The adsorbed species formed during adsorption of the reaction mixture, 5-hexen-2-one, chloroform and chloroform-*d* were followed by FT-IR measurements. The results are displayed in Figs. 3–5.

The IR spectrum of activated MgO (not shown) contains only a small, sharp adsorption band at 3745 cm^{-1} attributed to isolated OH groups on kinks or edges [31,32] and a broad band at 1400–1500 cm^{-1} with a shoulder at about 1600 cm^{-1} indicating the presence of residual surface carbonates. Exposure of the activated MgO to a mixture of 2-propanol/5-hexen-2-one 4/1 led to the spectrum shown in

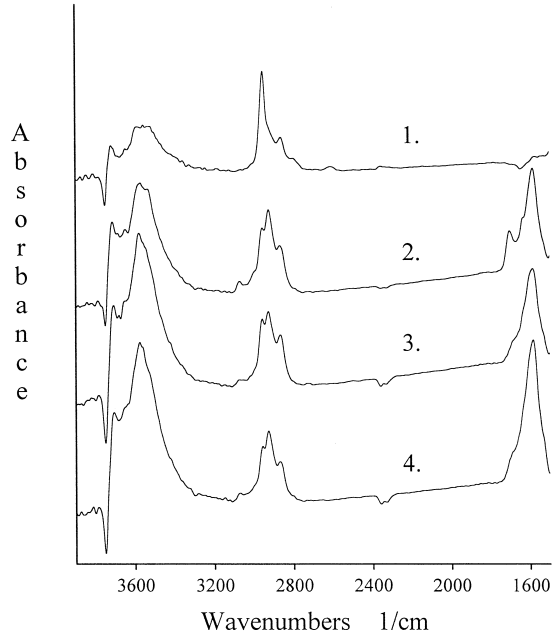

Fig. 3. FT-IR spectra of species formed on MgO activated at 673 K after treatment with 20 Torr of 2-propanol/5-hexen-2-one 4/1 mixture (**1**); followed by treatment with 5 Torr of 5-hexen-2-one (**2**); followed by treatment with 35 Torr chloroform (**3**); followed by treatment with 5 Torr of 5-hexen-2-one (**4**).

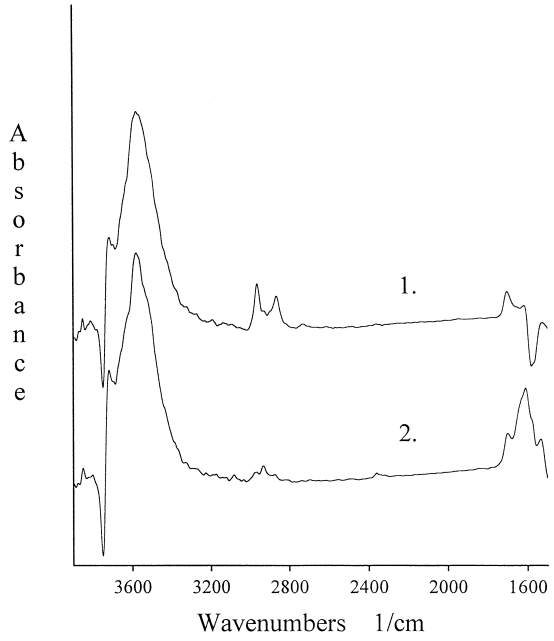

Fig. 4. FT-IR spectra of species formed on MgO activated at 673 K after treatment with 35 Torr chloroform (**1**); followed by treatment with 5 Torr of 5-hexen-2-one (**2**).

Fig. 3, **1**. As one can see the major bands are characteristic of the species formed by dissociative [ν(OH) at 3555 cm^{-1}, 3587 cm^{-1} and 3715 cm^{-1}; ν_{as}(CH) at 2956 cm^{-1}; ν_s(CH) at 2863 cm^{-1}; ν(CO) at 1164 cm^{-1} (not shown)] and by associative [ν(CO) shoulder at 1125 cm^{-1}] adsorption of 2-propanol due its significant excess in the mixture. Other bands can be assigned to the surface species formed by adsorption of 5-hexen-2-one [ν(=CH) shoulder around 3000 cm^{-1}; $\nu_{as}(CH_2)$ shoulder at 2930 cm^{-1}; $\nu_s(CH_2)$ at 2810 cm^{-1} and a small band at 1585 cm^{-1} attributed to carbonyl species strongly bound to the surface]. Adsorption of 5-hexen-2-one on this sample (Fig. 3, **2**) resulted in increase in the ν(OH) bands, decrease in the CH_3, increase in the CH_2 vibrational bands, significant increase in the shoulder due to ν(=CH) around 3000 cm^{-1} and appearance of the $\nu_{as}(=CH_2)$ band at 3080 cm^{-1}. At the same time the bands between 1100–1200 cm^{-1} almost completely disappeared (not shown). Important changes were detected in the region of the carbonyl vibrational bands, i.e., appearance of a sharp, intense band at 1585 cm^{-1} and a smaller band at 1705 cm^{-1}. These bands were identified as strongly and weakly bonded surface carbonyl species [16,31]. Adsorption of chloroform on this sample (Fig. 3, **3**) led to the increase in the bands in the ν(OH) region, especially the band at 3579 cm^{-1}. A slight decrease in the bands in the ν(CH) region and in the carbonyl region was observed too, especially of the band at 1705 cm^{-1}, which appeared only as a shoulder. Repeated adsorption of 5-hexen-2-one (Fig. 3, **4**) resulted in a similar spectrum to Fig. 3, **2**. However, the bands in the ν(OH) region (at 3579 cm^{-1}) and at 1585 cm^{-1} increased, while the band at 1705 cm^{-1} remained unchanged.

If, on a similarly activated sample chloroform was adsorbed first (Fig. 4, **1**) very intense bands appeared in the ν(OH) region at 3577 cm^{-1} and 3716 cm^{-1}, and the band of isolated OH groups decreased (negative peak at 3745 cm^{-1}). The

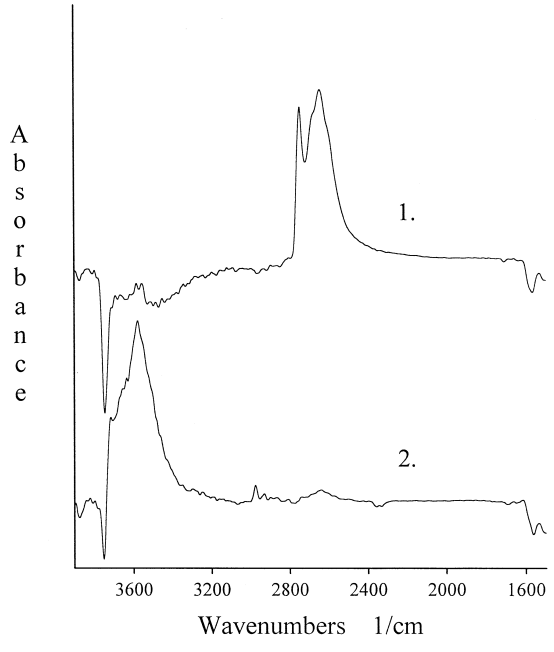

Fig. 5. FT-IR spectra of species formed on MgO activated at 673 K after treatment with 35 Torr chloroform-*d* (**1**); followed by treatment with 20 Torr of 2-propanol/5-hexen-2-one 4/1 mixture (**2**).

bands in the ν(CH) region can be assigned to small amounts of chloroform bonded via associative adsorption [16,33] and the bands at 1610 cm^{-1} and 1695 cm^{-1} to surface bidentate carbonate and bicarbonate [34]. Treatment of this sample with 5-hexen-2-one (Fig. 4, **2**) led to further increase in the ν(OH) band at 3579 cm^{-1} with relative decrease of the ν(OH) bands at lower wave numbers. In the ν(CH) region beside the disappearance of the bands characteristic of adsorbed chloroform, new bands with very low intensity appeared. As described above these bands are characteristics for adsorbed 5-hexen-2-one. In this spectrum important changes in the region of the carbonyl vibrations were detected. Here a band at 1585 cm^{-1} and a small shoulder at 1710 cm^{-1} appeared but not as intense as in the spectra from Fig. 3.

Adsorption of chloroform-*d* instead of chloroform on an activated sample (Fig. 5, **1**) led to disappearance of the vibrational band of the isolated OH groups and appearance of ν(OD) bands at 2747 cm^{-1} and 2643 cm^{-1} corresponding to isolated and to more acidic surface OD groups. No other bands could be detected in this spectrum, even in the ν(CD) region, leading to the conclusion that chloroform-*d* was adsorbed in a completely dissociated state. Exposure of this sample to a mixture of 2-propanol/5-hexen-2-one 4/1 led to the spectrum shown in Fig. 5, **2**. The ν(OD) bands almost completely disappeared and the ν(OH) bands reappeared but not at lower wave numbers than 3579 cm^{-1}. Very small bands also appeared in the ν(CH) region, at 1710 cm^{-1} and at 1585 cm^{-1}.

As an effect of the treatment of MgO with chloromethanes more active surface OH groups were generated, appearing at lower wave numbers in the IR spectrum. These groups take part in the reaction which is demonstrated by the disappearance of the OD bands during the reaction parallel with concomitant appearance of bands in the OH region with higher wave numbers than 3579 cm^{-1} (Fig. 5, **2**). In addition the decrease of the OH bands at lower wave numbers than 3579 cm^{-1} (Fig. 3, **4**) also supports this statement. The adsorption of the carbonyl group gave two characteristic bands at 1585 and 1705 cm^{-1}, which did not appear on samples treated with $CDCl_3$ (Fig. 5, **2**) and had very low intensity on samples treated with $CHCl_3$ (Fig. 4, **2**). The difference between the intensities of these bands in the two spectra may be due to the isotopic effect, supporting our assumption concerning the role of the surface OH(OD) groups in the reaction.

3.3. Reaction of chloromethanes with MgO

The surface reaction of dichloromethane, chloroform and carbon tetrachloride was studied in a pulse system and the results are collected in Fig. 6.

It was shown by GC-MS analysis that in each case the products obtained were CO and a small amount of CO_2. Beside the starting material no other chlorinated products were detected. Although using 1 μl pulses from each reagent led to different molar quantities, this did not influence decisively the total quantity of Cl^- adsorbed after 10 pulses. This was shown by the results obtained using 0.3 μl pulses of chloroform which gave a value close to the total Cl^- adsorbed in the previous case using 1 μl pulses. So, the total amount of Cl^- adsorbed after 10 pulses is almost independent of the quantities used in our experimental conditions, and is influenced mostly by the reactivity of the reagent. As one can see from Fig. 6 the treatment with carbon tetrachloride led to the smallest Cl^- quantity adsorbed and treatment with chloroform gave the highest amount of absorbed Cl^-.

These results are in agreement with the effectiveness of treatment with these chloromethanes on the stability of MgO during the CTH of 5-hexen-2-one (Fig. 2a). Treatment with chloroform proved to be the most effective in preventing MgO poisoning during CTH of 5-hexen-2-one (Fig. 2a) which can be explained by the highest amount of Cl^- adsorbed on the surface (Fig. 6). In the case of carbon tetrachloride

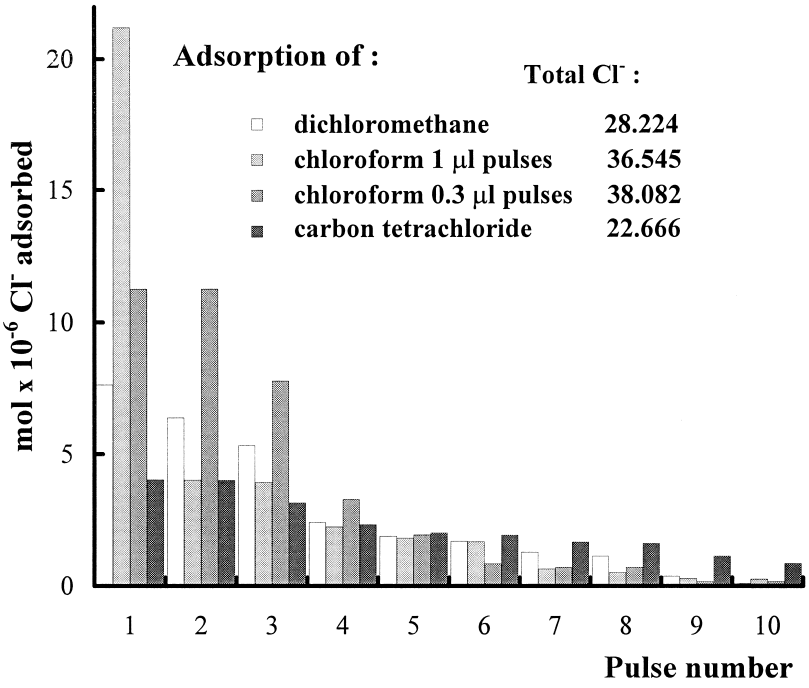

Fig. 6. Reaction of dichloromethane, chloroform and carbon tetrachloride on MgO (150 mg MgO, activation see Fig. 1a., reaction conditions: 20 cm^3 min^{-1} He, 523 K, pulses of 1 μl organochlorine reagent).

beside the smaller reactivity of MgO compared to that of chloroform, the absence of H in the molecule may be the cause of the poor performance to prevent poisoning. This proves the importance of generation of new, energetically proper surface OH groups, which can interact with the neighbouring Cl^- or O^{2-}. Their ν(OH) vibrations appear at 3579 cm^{-1}. These OH groups also appear after treatment with carbon tetrachloride, probably originated from the residual isolated surface OH groups.

4. Conclusions

During gas-phase CTH of 5-hexen-2-one using 2-propanol as hydrogen donor MgO was poisoned much faster than in the case of the corresponding saturated ketone, 2-hexanone. Treatment with organochlorine reagents prevented the poisoning of the catalyst. The C=C group from the alkyl chain was bonded to the surface Lewis acid sites, which led to strong adsorption of 5-hexen-2-one on the surface and as a consequence to a fast deactivation of MgO. This strong adsorption could be prevented by a treatment with chloromethanes. Treatment with chloroform was proved to be the most efficient in preventing MgO deactivation, due to its higher reactivity towards MgO surface which led to a higher Cl^- content of the catalyst and optimal quantity of active surface OH groups. As a result of treatment with chloroform we could optimize the experimental conditions to reduce an unsaturated ketone efficiently and selectively to the corresponding unsaturated alcohol in a continuous heterogeneous catalytic system.

After demonstrating the beneficial effect of treatment of MgO with chloromethanes and suggesting a reaction mechanism for CTH of saturated ketones with 2-propanol [15,16] in the present work we showed that this procedure is also applicable to the reduction of an unsaturated ketone. The results presented above confirmed the conclusions published earlier [16]

about the reaction mechanism of the gas-phase CTH of ketones with alcohols.

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