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STUDY OF THE MECHANISM OF ALDOL CONDENSATION OF ACETALDEHYDE IN ACIDIC AND BASIC CATALYTIC SYSTEMS

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To study the mechanism of the aldol condensation of acetaldehyde, $2MgO/SiO_2$ and $2ZrO_2*FeO*ZnO/SiO_2$ catalysts with a mass fraction of MgO and ZrO_2 of 2% were prepared, which had high catalytic activity and productivity and were selected for the process.

Physico-chemical properties of model systems. The surface ON groups of the model catalysts with high catalytic activity and productivity, selected for the process implementation, were studied by IR spectroscopy.

The IR spectrum of native silica contains a hot band at 3745 cm^{-1}, which is associated with isolated Si-OH groups. The addition of MgO and ZrO_2 oxides leads to a significant decrease in the intensity of this peak and its broadening towards the lower frequency range. This result may be due to the strong oxide-activator interaction with the formation of mixed oxides (=Si-OM =) on the support surface.

The main properties of the catalysts selected for the model, which have high catalytic activity and productivity, were studied by the TPD-CO2 method. The TPD-CO_2 curves for the catalyst samples $2ZrO_2*FeO*ZnO/SiO_2$ and SiO_2, which have high catalytic activity and productivity, selected for the production of divinyl from ethyl alcohol, are practically the same, except for a high temperature peak at 700 K for $2ZrO_2*FeO*ZnO/SiO_2$. For the catalyst selected for the process $2MgO/SiO_2$, which has high catalytic activity and productivity, a strong peak is observed at 373 K, which corresponds to the desorption of CO2 from weak basic centers. These data are in good agreement with the literature data. The main properties of activated oxides differ significantly from those of common MgO and ZrO_2 due to the high dispersion of SiO_2 activated oxides. This is due to the number of key centers on the surface of the catalyst selected for the process, which have high catalytic activity and productivity.

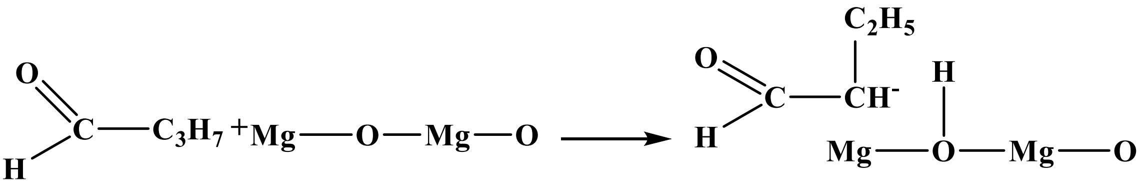
For the $2MgO/SiO_2$ system, intense lines corresponding to CO_2 adsorption at the main centers are observed in the 1450-1700 cm^{-1} wavenumber region, while for the $2ZrO_2{*}FeO{*}ZnO/SiO_2$ catalyst samples, the intensity of these lines is much lower.

According to the literature, these bands can be associated with vibrations of three types of surface species: bicarbonate, mono- and bidentate carbonate. The bands at 1709 and 1492 cm^{-1} are due to the interaction of weak basic OH groups on the 2MgO/SiO2H surface and are easily destroyed by bicarbonate when pumped at 373 K. $O=C=O$ represents the nonsymmetric and asymmetric vibrations of the bond. The 1673 cm^{-1} band may be associated with vibrations of bidentate carbonate particles formed on the surface of Lewis acid-base ion pairs. The 1610 and 1450 cm^{-1} bands may be associated with monodentate carbonate particles formed during the adsorption of CO_2 on isolated O_2- centers. Thus, the $2MgO/SiO_2$ catalyst, which has high catalytic activity and productivity, has three types of basic centers on the surface: strong basic centers represented mainly by isolated O_2- ions, medium-strength centers represented by Lewis acid-base pairs bound to Mg-O particles, and silicon oxide and weak basic OH groups.

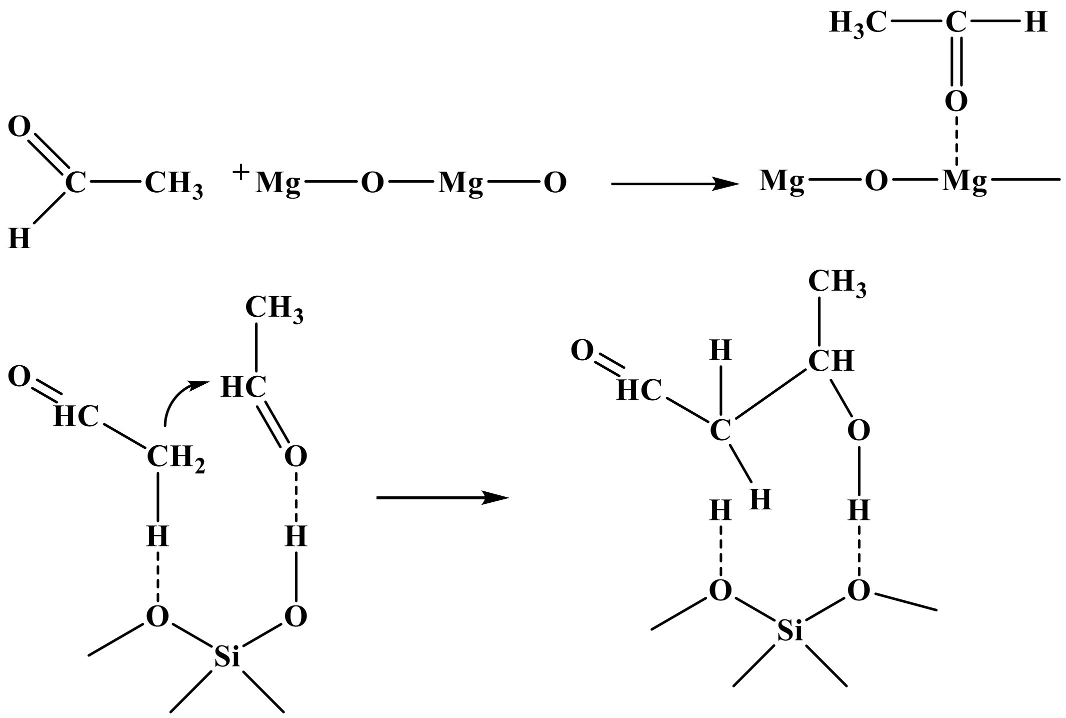
In contrast to the original SiO2, the appearance of new lines at 1608, 1491 and 1446 cm^{-1} is observed for the catalysts selected for the process, which have high catalytic activity and productivity, $2MgO/SiO_2$ and $2ZrO_2{*}FeO{*}ZnO/SiO_2$. These lines can be associated with the adsorption of pyridine at Lewis acid centers. The appearance of Lewis acid for activated zirconium oxide can be associated with the dehydroxylation of ZrO_2 after calcination. In $2MgO/SiO_2$, the Lewis acidity can be manifested by the coordinatively unsaturated Mg cations on the faces and edges of MgO crystallites. For the catalysts 2MgO/SiO2 and $2ZrO_2{*}FeO{*}ZnO/SiO_2$, which have high catalytic activity and yield, the selectivity for crotonaldehyde is slightly higher than for the $5MgO/SiO_2$ and $5ZrO_2{*}FeO{*}ZnO/SiO_2$ systems

(88 and 83%, respectively), which is associated with a decrease in the yield of the aldol condensation reactions. However, crotonaldehyde and acetaldehyde lead to the formation of heavy products. The method of selective poisoning of active centers was used to study the nature of the centers necessary for the aldol condensation reaction of acetaldehyde. We used carbonic anhydride as a molecular probe for the main centers, and pyridine was used to poison the acid centers. Under experimental conditions, these substances do not interact with acetaldehyde and do not affect the composition of the formed products. The initial rate of croton aldehyde formation was determined experimentally to compare the activity of catalysts selected for the process, which have high catalytic activity and productivity in the presence and absence of probe molecules.

The addition of CO_2 to the reaction mass does not lead to a change in the activity of the catalysts selected for the process, which have high catalytic activity and productivity, unlike pyridine, which leads to a significant slowdown of the reaction for both catalysts, which have high catalytic activity and productivity, which have been selected for the process. The significant decrease in the activity of the catalysts selected for the process, which have high catalytic activity and productivity, with the addition of pyridine indicates that Lewis acid centers play an important role in the aldol condensation of acetaldehyde at acidic and basic centers. CO_2 adsorption led to a significant decrease in activity, while ammonia adsorption did not affect the activity. This fact can be explained by the different activation mechanisms of acetaldehyde and butyral. The removal of a proton from the secondary carbon atom of butyral should occur more easily at the main centers of magnesium oxide than the removal of a proton from the primary carbon atom of acetaldehyde:

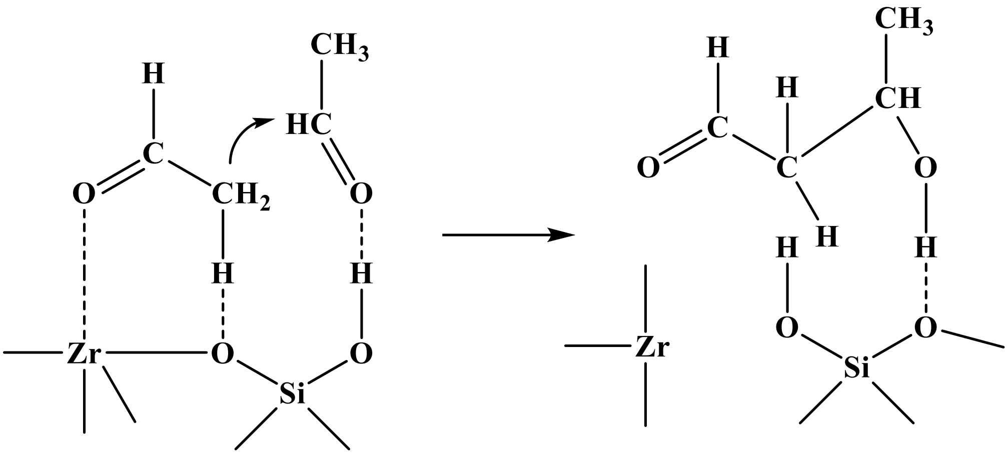


It can be assumed that the activation of acetaldehyde at Lewis acidic centers leads to the easy separation of a proton from acetaldehyde:



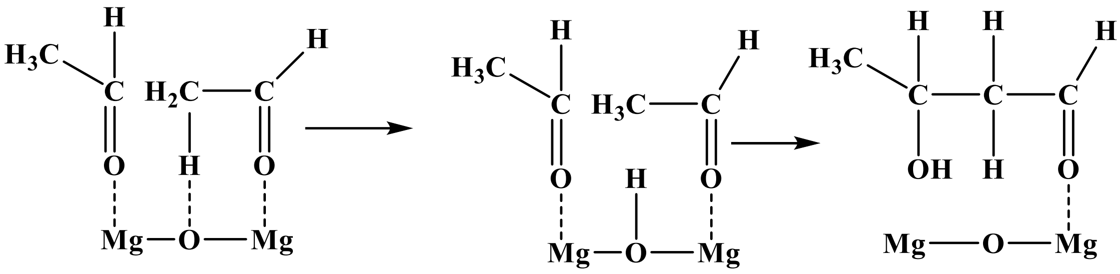
Further increase in temperature does not lead to a change in the spectra.

To study the role of acidic and basic centers in the condensation reaction of acetaldehyde to crotonaldehyde, the reaction was carried out with CO_2 and pyridine pre-adsorbed on them on catalysts with high catalytic activity and yield, selected for the process, which have high catalytic properties and yield, on catalyst samples selected for the production of divinyl from ethyl alcohol. The initial adsorption of carbonic anhydride does not lead to a change in the intensity and position of the adsorbed acetaldehyde peaks, while the adsorption of pyridine leads to a significant decrease in the intensity of the lines and inhibition of the crotonaldehyde formation reaction over the entire temperature range. As a result, the initial adsorption of pyridine leads to a weakening of the binding of acetaldehyde to the surface and stops the aldolization process. Thus, the obtained spectral data confirm the hypothesis of the participation of Lewis acid centers and surface groups in the reaction and show an increase in the activity of $2ZrO_2*FeO*ZnO/SiO_2$ relative to SiO_2. Based on the obtained data, the following mechanism of aldol condensation of acetaldehyde on $2ZrO_2*FeO*ZnO/SiO_2$ can be proposed.



According to this mechanism, the introduction of zirconium oxide into silica leads to the formation of Lewis acid centers and an increase in the Brønsted acidity of silanol groups. The catalyst selected for the process, $2ZrO_2$*FeO*ZnO/SiO_2, which has high catalytic activity and productivity, is almost completely converted to acetaldehyde at 373K, while the catalyst selected for the process, 2MgO/SiO_2, which has high catalytic activity and productivity, is not completely converted even at 453K.

Strong interaction of acetaldehyde with Si-OH. may be the result of the induction of acidity of silanol groups upon interaction of the centers $-\boldsymbol{Mg}-\boldsymbol{O}-\boldsymbol{Si}-\boldsymbol{OH}$ with CO2:



The results obtained show that the strong basic centers located on the surface of the 2MgO/SiO_2 catalyst, which has high catalytic activity and productivity, are more active than the Lewis centers of the $2ZrO_2$*FeO*ZnO/SiO_2 catalyst, which has high catalytic activity and productivity, and is selected for the process.

However, they are quickly quenched and then the reaction proceeds in the form of a “Lewis center - weak base” ion pair, similar to the mechanism described for $2ZrO_2$*FeO*ZnO/SiO_2. To verify this, experiments on the initial adsorption of pyridine on $2MgO/SiO_2$ catalyst samples were carried out (Fig. 6.10). As in the case of $2ZrO_2*FeO*ZnO/SiO_2$, the initial adsorption of pyridine leads to the almost complete disappearance of the peaks corresponding to the bond vibrations in acetaldehyde and crotonaldehyde, which indicates the participation of Lewis acid centers in the condensation reaction of acetaldehyde. Thus, studies using IR spectroscopy show that the aldol condensation reaction of acetaldehyde can proceed by two mechanisms on the $2MgO/SiO_2$ catalyst chosen for the process, which has high catalytic activity and productivity:

a) basic mechanism, including carbanion formation at strong basic centers and

b) Synchronous mechanism involving activation in "Lewis center - weak base" pairs.

The synchronous mechanism is likely to occur under the reaction conditions of the flow reactor designed for the process on the $2ZrO_2*FeO*ZnO/SiO_2$ and $2MgO/SiO_2$ catalysts with high catalytic activity and productivity, which is in good agreement with the data on the selective poisoning of the catalysts with high catalytic activity and productivity by the addition of probe molecules.

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