JOURNAL OF CATALYSIS 42, 205–212 (1976)

Catalytic Dehydration of Secondary Alcohols over Thoria: Infrared Study and Generalization to Basic Catalysts

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Received February 10, 1975; revised September 19, 1975

Infrared studies of adsorbed 2-hexanol and 1-d_3-2-hexanol over thoria show that secondary alcohols are dehydrated on this catalyst via a surface alcoholate. A study of dehydration of 2-hexanol and *cis*-2-methylcyclohexanol over typical basic catalysts, alkaline earth oxides, gives results in selectivity which can be explained by an E_1cB-type mechanism, the role of the basic centers being preponderant.

Catalytic dehydration of alcohols provides a good model for elimination reaction mechanisms in heterogeneous systems, as well as an activity scale for catalysts with acidic properties (*1*, *2*).

Numerous oxides are good catalysts for alcohol dehydration yielding either olefins or ether (*3*), the best known being certainly alumina. Dehydration to olefins on this catalyst has been shown to consist in a concerted *trans* elimination with an E_2-like mechanism (*4*); Knözinger (*5*) has proved that olefin formation from primary and secondary alcohols can proceed through several paths, with or without an intermediate ether, the latter being preponderant at low temperature.

Thoria is also a good catalyst for dehydration of alcohols (*6*) but it has particular properties in that ether oxide is not an intermediate in the reaction path (*7*) and secondary alcohols of the R–CHOH–CH_3 type are dehydrated with very good selectivity to yield terminal olefins (*8*, *9*).

In earlier papers (*10*, *11*), it was shown that the particular properties of thoria with secondary alcohols can be explained by the basic character of the surface. To define more accurately the mechanism, the adsorption of R–CHOH–CH_3 type secondary alcohols has been studied over thoria by means of infrared spectroscopy. This allows a more precise characterization of the adsorbed species.

The present study reports also the dehydration of 2-hexanol and *cis*-2-methylcyclohexanol on alkaline earth oxides. The results obtained using these model systems on the basic catalysts lead us to conclude that our earlier results with thoria are typical of the general class of basic catalysts.

EXPERIMENTAL METHODS

Catalysts

Thoria used for infrared studies was obtained by calcination of hydroxide, as described previously (*12*). Infrared wafers (18 mm diameter, 40–50 μm thickness) of thoria were pressed at 6 T cm^{-2} of wafer.

All alkaline earth hydroxides have been prepared by hydration of the oxides, as described by Baird and Lunsford for MgO (*13*). The hydroxides were obtained by boiling for 2 hr a suspension of oxide in deionized water, filtering with a Buchner funnel and drying for 24 hr at 150°C. The catalyst so obtained was used after sieving, the only particles retained being those with sizes between 0.08 and 0.125 mm.

Apparatus

Infrared spectra have been recorded on a Perkin-Elmer spectrometer Model 125 or 457, at room temperature. The double beam mode was used and the transmittance was recorded as a function of wavenumber. Catalyst wafers were introduced in an aluminum holder which was placed in a Pyrex cell. At the upper end, two KBr windows were sealed on both sides and a stopcock allowed different treatments to be applied. Alcohols were admitted under their own vapor pressure at room temperature from a vacuum-sealed tube, after drying on a 4A molecular sieve.

Reactions with basic catalysts have been performed in a fixed bed integral reactor (*14*) and reaction products were analyzed by vapor phase chromatography (*10*).

Reactants

2-Hexanol (Aldrich Chemical Co) with a purity of 99% was used without any further purification.

cis-2-Methylcyclohexanol was prepared by hydrogenation of 2-methylcyclohexanon on platinum black in acetic acid solution (*15*); after two cycles of preparative vapor phase chromatography on a diglycerol column, the purity of the alcohol was improved to 99.9%.

1-d_3-2-Hexanol was obtained by means of Grignard synthesis from CD_3I and valeraldehyde. It was used after a preparative vapor phase chromatography purification on a Carbowax 1500 column. Its isotopic purity, determined by mass spectrometry, was 96%.

RESULTS

INFRARED STUDY OF THE ADSORPTION ON THORIA

The catalyst ir spectrum, recorderd after evacuation of 15 hr at 300°C under 10^{-5} Torr, shows, beside the classical carbonate bands on this catalyst (*16*), three O–H bands, respectively, at 3710, 3640, and 3520 cm^{-1} (Fig. 1a). In the 3800–3500 cm^{-1} region, the spectrum is very similar to that of alumina described by Peri (*17*) and Dunken and Fink (*18*).

When 2-hexanol is adsorbed on the catalyst kept at 300°C, the spectrum is modi-

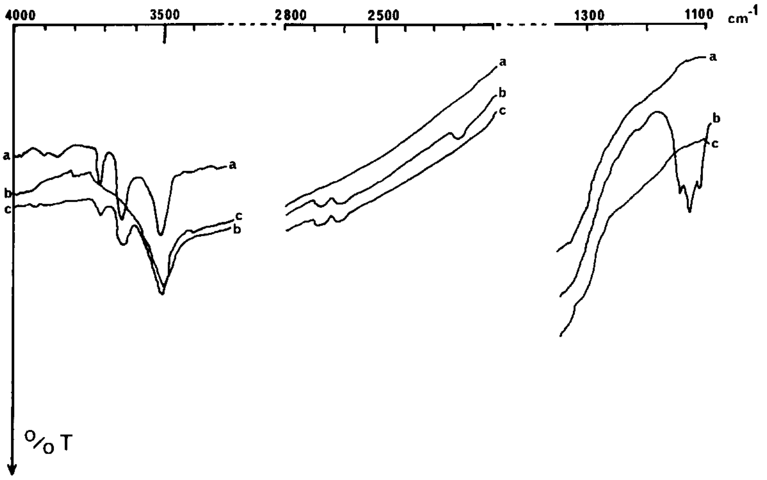


FIG. 1. Infrared spectra of 1-d_3-2-hexanol adsorbed on thoria: (a) Catalyst spectrum after 15 hr outgassing at 300°C. (b) Spectrum of 1-d_3-2-hexanol adsorbed after a treatment of 1 hr at 250°C. (c) Spectrum after a treatment of 15 hr at 300°C.

fied in the O–H stretching region; the first two bands at 3710 and 3640 cm^{-1} are strongly attenuated while the third one, at 3520 cm^{-1}, is only slightly modified or not modified at all. Moreover, in the 1200–1000 cm^{-1} region, an additional band appears in the C–O vibration region. The liquid 2-hexanol spectrum shows two bands at 1150 and 1115 cm^{-1}, but in the adsorbed state these two bands are changed into three, at 1150, 1135, and 1115 cm^{-1}. Desorption of the alcohol under vacuum for 1 hr at increasing temperature does not change the spectrum. It is only when heated to 250°C that the O–H catalyst band at 3640 cm^{-1} is recovered. The initial catalyst spectrum shows up after 15 hr at 300°C under vacuum.

The adsorption of 2-hexanol perdeuterated on the first carbon leads to the same results; the two first O–H stretching bands at higher frequencies disappear but the additional band at 1130 cm^{-1} is present (Fig. 1b). For the adsorbed alcohol, the C–D band at 2225 cm^{-1} is weaker than the one obtained with liquid alcohol. One hour desorption treatment under vacuum at increasing temperatures results in a progressive decrease in the band intensities of the adsorbed alcohol without any change in their positions. On the other hand, when the O–H bands at 3710 and 3640 cm^{-1} reappear, two small bands at 2690 and 2625–2630 cm^{-1} become visible (Fig. 1b). As for 2-hexanol, a 15 hr treatment under vacuum at 300°C removes the adsorbed alcohol spectrum. Nevertheless, the 3710 and 3640 cm^{-1} O–H bands are less strong than in the initial catalyst spectrum and the bands at 2690 and 2630 cm^{-1} persist (Fig. 1c). These two bands might be ascribed to O–D surface groups formed by the dehydration of adsorbed alcohol into olefin. Indeed, if we assume in first approximation, that the binding force constant is independent of the isotope, calculations show that the 3710 and 3640 cm^{-1} bands must be near 2700 and 2650 cm^{-1} when a deuterium atom takes the place of a hydrogen atom.

STUDY OF ALKALINE EARTH OXIDES AS CATALYSTS

On all these catalysts, water formed by dehydration of alcohols can irreversibly hydrate the active oxide into hydroxide. To avoid this, the initial hydroxide is heated under nitrogen inside the reactor up to the desired temperature for the reaction. The rehydration of these oxides at room temperature and normal atmosphere is an irreversible and very fast reaction, and therefore the specific area and the porosity of these different samples could not be determined. Nevertheless, the results obtained, in particular for CaO, can be usefully compared to those obtained by Iisuka *et al.* (*19*).

a. 2-Hexanol Dehydration

On all the alkaline earth oxides studied (MgO, CaO, SrO and BaO), the most important reaction is the dehydrogenation of alcohol into ketone, dehydration being a secondary reaction. Nevertheless, if 2-hexanol is flowed over the catalyst (alcohol pressure = 0.2 atm, nitrogen pressure = 0.8 atm) the temperature being progressively increased, the 1-hexene percentage in the olefinic fraction (i.e., selectivity) can be plotted versus reaction temperature for the different catalysts. In Fig. 2, it can be seen that 1-hexene selectivity increases at a temperature which is typical for each studied oxide; this characteristic temperature corresponds to the hydroxide to oxide dehydration (*20*). Maximum values of selectivity vary according to the catalysts, i.e., 63% on MgO, 82% for CaO, and only 54% with SrO. For BaO, however, it is impossible to reach the maximum possible value for selectivity because the melting point of $Ba(OH)_2$ is too low. With the type of apparatus used here, which is made of Pyrex glass, it is not possible to go over 550°C.

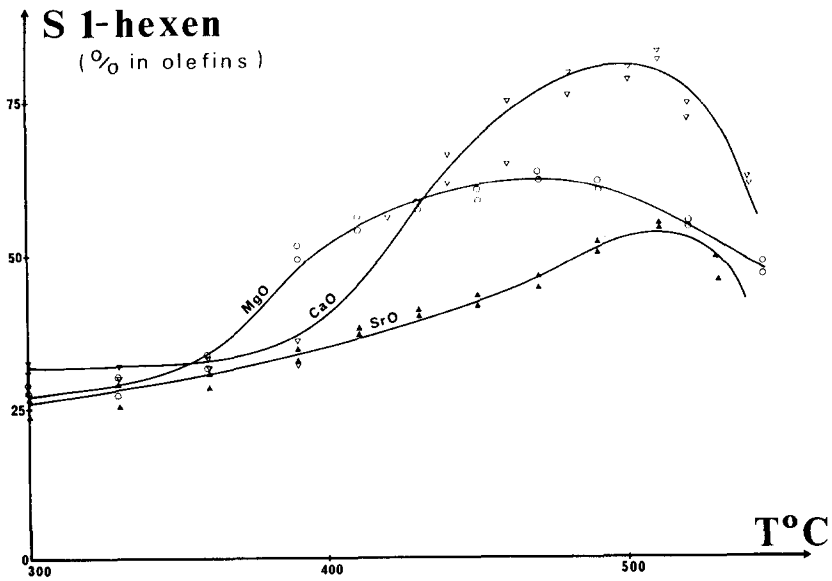


FIG. 2. Dehydration of 2-hexanol over alkaline earth oxides: dependence of 1-hexene selectivity on temperature of reaction.

Results obtained with CaO can be compared to those of Iisuka *et al.* (*19*). When the selectivity in 1-hexene together with the basicity of the catalyst are plotted versus temperature on the same graph (Fig. 3), it can be seen that the two curves are in good correspondence with each other.

Over thoria, the addition of ammonia, because of a poisoning of surface acidic

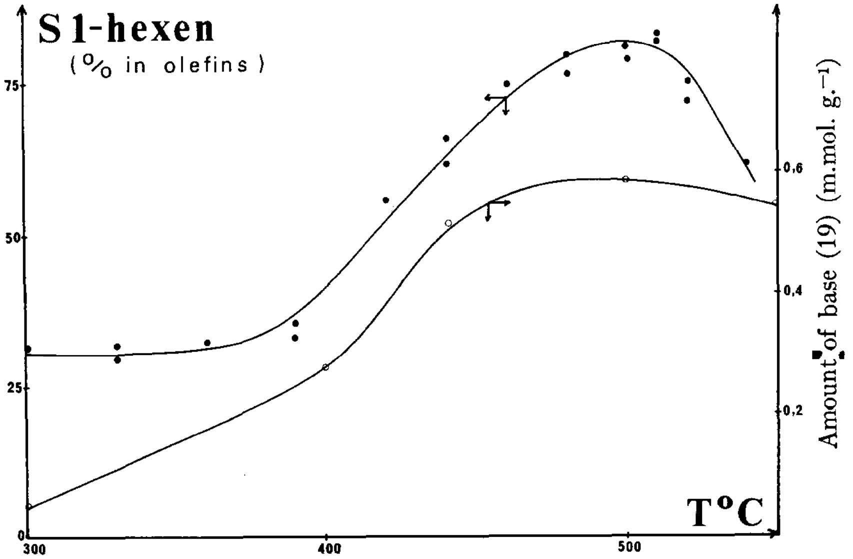


FIG. 3. Relation between 1-hexene selectivity and basicity of CaO with reaction or calcination temperature.

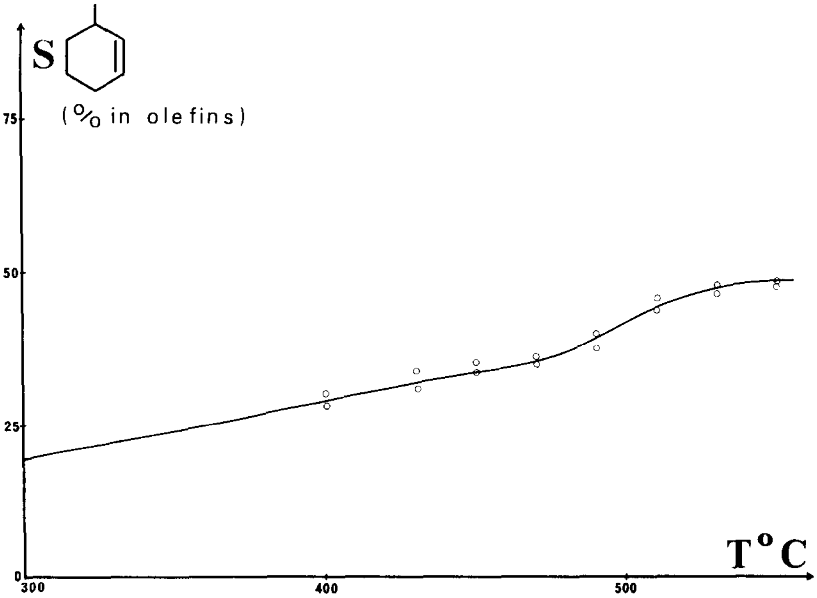


FIG. 4. Dehydration of 2-methylcyclohexanol over CaO. Changes in 3-methylcyclohexene selectivity with reaction temperature.

centers, could have a pronounced effect on the activity and selectivity of the catalyst, according to the preparation mode (*10*). This effect, however, could not be observed on alkaline earth oxides; the addition of ammonia (ammonia pressure = alcohol pressure = 0.2 atm, nitrogen pressure = 0.6 atm) to CaO at 510°C had no effect, the selectivity in 1-hexene remaining 82%. Therefore, this good selectivity for R—CH═CH_2 olefin types may not be due to the presence of possible strong acidic centers on the surface, but rather the result of the catalyst basicity.

b. cis-2-*Methylcyclohexanol Dehydration*

Dehydration of this alcohol in the same conditions as 2-hexanol gives the same kind of curves. On Fig. 4, the 3-methylcyclohexene percentage in olefins is plotted versus the temperature reaction for calcium oxide; the selectivity is lower than with 2-hexanol. Here again, ammonia has no effect on the selectivity. Curves for the three studied catalysts (MgO, CaO and SrO) are of the same kind.

DISCUSSION

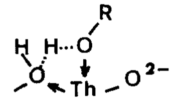
Infrared studies of adsorbed 2-hexanol at 300°C over thoria show that the O–H alcohol band disappears when adsorbing alcohol. The infrared spectrum obtained in this way is nearly the same as that of thorium isopropoxide (*21*), and in the 1200–1000 cm^{-1} region, the bands observed are approximately the same as that observed when secondary alcohols are adsorbed over alumina (*22*) or titanium oxide (*23*) at low temperature. It is not possible to see any change in the band positions of the adsorbed alcohol when the catalyst is kept at 300°C, whereas similar studies with primary and secondary alcohols over alumina (*22–24*) or hydroxyapatite (*25*) show characteristic bands for carboxylate surface groups. Moreover, it is possible to see thorium alcoholates by means of infrared spectroscopy when esters are adsorbed on thoria (*26*).

When 2-hexanol is adsorbed on thorium oxide, the first two O–H bands of the catalyst, at 3710 and 3640 cm^{-1}, are strongly attenuated. The frequency differences between the surface O–H groups can be understood on the basis of a different local environment: the more surrounded they are with O^{2-} ions, the more basic they are and the higher is their vibration frequency (*17*).

The formation of surface alcoholate may be interpreted as adsorption of an alcohol molecule on a surface O–H group, the alkoxy radical taking the place of the hydroxy group:

$$R\text{-}OH + O^{2-}\,\overset{OH}{\overset{|}{Th}}\,O^{2-} \rightleftharpoons H_2O + O^{2-}\,\overset{O^{\diagup R}}{\overset{|}{Th}}\,O^{2-}$$

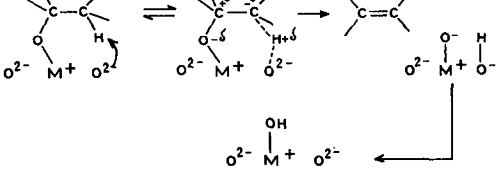
To explain the disappearance of bands due to free surface hydroxyl groups when the surface is covered by alcohol molecules, another possibility exists which is an interaction via coordinative adsorption on exposed Th^{4+} ions and lateral interaction of the alcohol molecule with the O–H group. This has been previously discussed by several authors (*27*, *28*):



In this case, the primary interaction is between the alcohol hydroxyl oxygen and a Lewis acid site. However, results obtained by poisoning the surface of thoria with NH_3 (*10*) ruled out the possibility of strong acidic centers participating in the selective dehydration of 2-hexanol into 1-hexene and of *cis*-2-methylcyclohexanol into 3-methylcyclohexene. When dehydration is very selective, the only acidic centers which could participate in the catalytic reaction are those which are very weak because they are not poisoned by NH_3. Moreover, previous work showed that the surface of thoria carried between 80 and 100% of a hydroxyl monolayer (*29*) for the conditions used in this study. Therefore, the adsorption with dehydration and formation of a surface alkoxy group is likely to be the best way of explaining the results obtained with thoria.

Concerning the selectivity in olefins of the dehydration reaction, three mechanisms are possible in elimination reactions over polar catalysts (*30*). The E_1 type can be ruled out because of the nature of the catalysts used; the surface does not have the strong acidic centers which are required for eliminations of this type. A *cis* or *trans* E_2 elimination is possible over these catalysts (*9*, *31*), but in this case, it is difficult to understand why such mechanisms with secondary alcohols of $R\text{–}CHOH\text{–}CH_3$ type lead to olefins with a Saytzeff distribution over alumina (*4*), hydroxyapatite (*32*) or metal salts (*33*) and with a Hofmann distribution over thoria or alkaline earth oxides.

The preferential formation of 1-hexene from 2-hexanol over alkaline earth oxides may be connected with the basicity of the catalyst, as shown in Fig. 3 for calcium oxide. Over thoria (*10*), selectivities observed in dehydration of secondary alcohols can be well explained assuming two parallel mechanisms; a *trans* E_2 elimination which is poisoned by NH_3, leads to the more substituted olefin and an E_1cB mechanism which can be related to the amount of basic centers, leading to the less substituted olefin. With the studied alkaline earth oxides, as in the case of thoria, the presence near the adsorbed alcoholate of strong basic O^{2-} ions from the crystalline structure (*34*) allows an attack on the hydrogen of the adsorbed molecule:



In this case, the transition state is nearly the same as that proposed for E_1cB elimination reactions (*35*). By a rearrangement of this intermediate an olefin can be obtained, and the O–H surface group may be reformed with one hydrogen of the organic molecule; if deuterium replaces hydrogen, the dehydration will lead to O–D surface groups. According to this mechanism, the dehydration selectivity in olefin depends on the attack of the hydrogen by a basic center, and the more substituted α-carbon of the alcohol function, the stronger must be the basic center for the hydrogen abstraction. With 2-hexanol, the hydrogen of the methyl group is about 100 times more labile than that of the third secondary carbon atom. With a catalyst which does not have too strong surface basic centers, this alcohol dehydration will be very selective for the 1-hexene formation. This is in fact observed in the case of thoria. When the strength of the basic center increases, the selectivity in terminal olefin decreases because the attack on the β-hydrogen can occur on primary and secondary hydrogen. So, if the highest selectivity value for CaO is near 80% for the 1-hexene formation, for SrO which is more basic than CaO, this value drops to 56%.

Another possibility for the loss in selectivity with 2-hexanol between CaO and SrO is the size of the cations. Sr^{2+} is larger than Ca^{2+} and the screening effect of O^{2-} ions is lower with SrO (*30*), so with this latter catalyst an E_2 mechanism leading to 2-hexene would be easier, the acidic centers being more exposed.

At temperatures higher than 510°C for CaO, the selectivity in 1-hexene drops to lower values. This fact may be correlated with the formation of acid centers (Ca^{2+}, Sr^{2+}) on the surface when decomposition of carbonate-like species occurs at these temperatures, as recently reported by Hattori *et al.* (*36*).

With *cis*-2-methylcyclohexanol on these catalysts, the attack by a basic center takes place on a secondary hydrogen, the olefin formed being 3-methylcyclohexene, or on the tertiary hydrogen with formation of 1-methylcyclohexene. As the acidity difference of these two hydrogens is about 10 times weaker than in the case of 2-hexanol, selectivity differences are less clear than with the linear alcohol and all the alkaline earth oxide catalysts studied have strong basic centers which can induce an attack on a tertiary hydrogen.

According to this mechanism, thoria appears in secondary alcohol dehydration as a catalyst with weak basic centers.

ACKNOWLEDGMENT

The authors express their grateful appreciation to Professor H. Knözinger for interest and valuable discussions about this paper.

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