Novel isomerization of ω-phenylalkanals to phenyl alkyl ketones over cesium (lanthanum) oxide supported on mesoporous aluminosilicate molecular sieves and related materials

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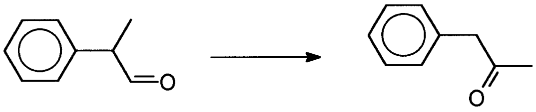
A novel rearrangement of the ω-phenylalkanals phenylacetaldehyde, 3-phenylpropionaldehyde and 4-phenylbutyraldehyde towards phenyl alkyl ketones is reported. The liquid-phase isomerizations are catalyzed by cesium oxide or binary cesium–lanthanum oxide supported on the mesoporous aluminosilicate molecular sieves MCM-41 and HMS and on amorphous supports like silica–alumina and γ-alumina. Beside the title reaction the aldol condensation is observed as a side-reaction. A mechanism is proposed in which the aromatic ring is involved in the rearrangement process. Factors governing the activities and product selectivities are presented.

Keywords: ω-phenylalkanals, phenyl alkyl ketones, rearrangement, base catalyses, MCM-41 and HMS

1. Introduction

Aldehyde isomerization over solid catalysts is an interesting and attractive route to ketones [1]. Some examples of branched-aldehyde isomerizations over different types of catalyst have been reported. The pentasil zeolites B-MFI and Fe-MFI are active at high temperature (400°C) in this reaction and show high selectivities to the corresponding ketones [1,2]. A less selective catalyst is the K_2CO_3-promoted CrZnMn-oxide system [3]. In this case the reactions were also carried out in the gas-phase at high temperatures and water vapour was added [1–3]. In contrast to the radical mechanism proposed for the latter case [3], the mechanism of the aldehyde–ketone isomerization over pentasil zeolites is proposed to occur exclusively via an α-methyl, α-phenyl or α-benzyl shift [1], because a hierarchical order in R-shift was observed for aromatic aldehydes over pentasil zeolites. Rearrangement of 2-phenylpropanal gave a methyl shift instead of a phenyl shift which results in the selective formation of phenylacetone [1,2]:



Recently we reported on the strongly basic properties of cesium oxide supported on MCM-41 [4,5], a mesoporous molecular sieve of the M41S family [6]. A disadvantage of this system was the poor regenerability which was reflected by a loss in surface area and by clustering of the oxide particles [5]. We succeeded to improve the thermal stability substantially and to lower its moisture sensitivity by addition of equimolar amounts of lanthanum which gave the MCM-41 supported binary cesium–lanthanum oxide [7]. In spite of their mild basicity these CsLa / MCM-41 materials showed an interesting performance in the liquid-phase Michael addition of ethyl cyanoacetate to ethyl acrylate under mild conditions [7].

Here we report on the unexpected behaviour of the binary CsLa-oxide supported on mesoporous aluminosilicate MCM-41 [6] and HMS [8] materials, and on an amorphous silica–alumina (ASA) support in the presence of aromatic aldehydes in the liquid phase. All these basic catalysts rearranged selectively the ω-phenylalkanals to phenyl alkyl ketones in the liquid phase. Factors like basicity and the presence of mesopores have an influence on the activity and selectivity to the phenyl alkyl ketone and the α,β-unsaturated ketone, a by-product resulting from the aldol condensation. A tentative mechanism is advanced which explains the novel rearrangement.

2. Experimental

2.1. Materials

The mesoporous aluminosilicate MCM-41 and HMS materials having both a Si / Al ratio of 15 were prepared according to the literature procedures of ref. [7] and ref. [8], respectively. The amorphous silica–alumina (ASA) supports were kindly donated by Akzo Nobel Chemicals Amsterdam, The Netherlands. These are a low alumina containing ASA (LA-SHPV; denoted as ASA1) with

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12.0% of Al_2O_3 and a high alumina containing ASA (HA-SHPV; denoted as ASA2) with 25.0% of Al_2O_3. The ASAs were prepared, according to the manufacturer, by precipitating alumina on silica particles. The γ-Al_2O_3 was purchased from Merck.

The supported CsLa-oxide materials were prepared as follows. A mixture containing 5 g of the support, 5 wt% Cs (added as cesium acetate, ACROS), an equimolar amount of lanthanum nitrate hexahydrate (Merck) and 10 g of methanol was stirred at room temperature. After 3 h the methanol was evaporated quickly under vacuum and the material was subsequently calcined at 500°C for 5 h. The cesium oxide containing materials were prepared in the same way except that lanthanum nitrate was omitted. Both MCM-41 and HMS were Na^+ ion-exchanged in a 1 M NaCl aqueous solution at 60°C overnight, and the materials obtained will be denoted as Na-MCM-41 and Na-HMS, respectively. The acid sites of the two ASA supports and that of γ-Al_2O_3 were neutralized with 0.1 M NaOH aqueous solution, washed and dried prior to the metal salt-impregnation.

2.2. Techniques

Structural characterization was performed by powder X-ray diffraction on a Philips PW 1840 diffractometer using monochromated Cu Kα radiation. Patterns were recorded from 1° to 40° (2θ) with a resolution of 0.02° and a count time of 1 s at each point.

Temperature-programmed desorption (TPD) of carbon dioxide was performed on a Micromeritics 2900 TPD/TPR instrument. The calcined materials were first activated at 600°C for 5 h and subsequently cooled down to 110°C under a helium flow. Then the activated materials were saturated with dry gaseous carbon dioxide at this temperature. Physisorbed carbon dioxide was removed by purging under a helium flow at 110°C until a stable baseline was monitored (about half an hour). The TPD was performed under a helium flow (10 ml/min) by heating from 110 to 600°C with a heating rate of 10°C/min.

Multipoint BET surface areas, pore volumes and pore size distributions of a number of materials were calculated from N_2 adsorption/desorption isotherms at −196°C using a Quantochrome Autosorb 6 apparatus. The samples were outgassed for 16 h under vacuum at 350°C prior to use.

2.3. Catalysis

Phenylacetaldehyde, phenylacetone and 2-phenylpropionaldehyde were purchased from Aldrich and 3-phenylpropionaldehyde from Merck. All the commercial reactants were distilled prior to use. The non-commercially available reactants 4-phenylbutyraldehyde and 2-(4-methoxyphenyl)acetaldehyde were prepared according to ref. [9] from the corresponding primary alcohol purchased from Fluka and Aldrich, respectively, by using oxalyl chloride and dimethyl sulfate. The 2- and 3-methoxy-substituted phenylacetaldehydes and 2,6-dichlorophenylacetaldehyde were prepared according to ref. [10] from the corresponding benzyl cyanide purchased from Aldrich and ACROS.

The pre-activated catalysts (1 wt% with respect to the total amount of aldehyde) were allowed to react with 5 g of the ω-phenylalkanal in a dry glass reactor at 100°C under air. No solvents were applied. The course of the reaction was monitored by GLC using a capillary CP sil5 column. Aliquots were taken at suitable time intervals and were analyzed by GC-MS. Products were isolated by vacuum distillation or column chromatography and characterized by ^1H and ^{13}C NMR.

3. Results

3.1. Catalysis

Studying the conversion of phenylacetaldehyde over the supported cesium oxide and binary cesium–lanthanum oxide catalysts containing 5 wt% Cs and 10 wt% CsLa (Cs : La atomic ratio = 1 : 1), respectively, in the solvent-free procedure at 100°C two main products,

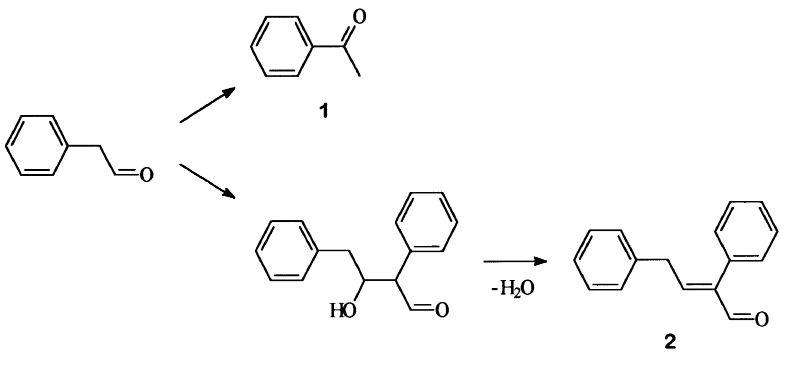

Figure 1. The reactions of phenylacetaldehyde over Cs and CsLa-oxide containing catalysts.

acetophenone (**1**) and 2,4-diphenyl-2-butenal (**2**), were observed (figure 1). The presence of acetophenone implies an isomerization of phenylacetaldehyde, whereas **2** will be formed by the commonly encountered base-catalyzed self-aldol condensation leading to 2,4-diphenyl-3-hydroxybutanal followed by dehydration (figure 1). In all cases traces of ethylbenzene were observed.

Table 1 illustrates the performance of various basic catalysts in the liquid-phase conversion of phenylacetaldehyde. All the catalysts tested are very active systems as indicated by the specific activity A_{wt} expressing the number of mmol substrate converted per gram catalyst per hour. The Al_2O_3 and the high alumina containing ASA2 systems show the highest activities, but the selectivities to the by-product ethylbenzene are in both cases substantial. It was checked that in the absence of a catalyst no conversion is occurring. Considering the mesoporous catalysts it can be noticed that the most active catalyst is Cs/MCM-41. The cesium analogue Cs/HMS shows a lower activity, but a largely improved selectivity to acetophenone. A worsening rather than an improvement of the activity was achieved when the extraframework H^+ ions were ion-exchanged with Na^+ ions. A similar phenomenon was observed for MCM-41 although the decrease in activity here is much less. Therefore it is suggested that the cesium oxide particles are most probably situated near the aluminum sites of the framework and that Na^+ ions influence the basicity of the supported metal oxides (vide infra).

Generally the basicity of the supported CsLa-oxides is lower than that of the Cs-oxide analogues (as shown by CO_2-TPD) [7]. Consequently the activities of the CsLa-oxide systems are lower than those of the Cs-oxide ones. In general the mesoporous Cs- and CsLa-oxide catalysts show a higher selectivity to acetophenone **1** than to the more bulky α,β-unsaturated aldehyde **2**. The HMS systems show even a larger preference in producing **1**. Cs/ASA2 is exceptional in showing a very low selectivity to **2** together with a high selectivity to **1**. Ethylbenzene is produced as a minor product except over Cs/Al_2O_3 and Cs/ASA1. The MCM-41, HMS and ASA1 supported CsLa-oxides produced hardly any ethylbenzene.

The conversion of 3-phenylpropionaldehyde is also depicted in table 1. Generally, this reaction proceeds more slowly than that of phenylacetaldehyde which is reflected by the lower A_{wt} of the catalysts. In line with the previous reaction, mainly propiophenone, **3**, and the dehydrated aldol product 2-benzyl-4-phenyl-2-butenal, **4**, are produced (figure 2). Besides, very small amounts of propylbenzene are noticed. Remembering the considerable high specific activity of ASA2 and Al_2O_3 systems in the conversion of phenylacetaldehyde here the catalysts show activities which differ actually not very much from those of the other catalysts. Within the supported Cs-oxide series, the Cs/HMS and Cs/Na-HMS materials show, beside the lowest A_{wt}, a high selectivity to the α,β-unsaturated aldehyde **4**.

Finally in this series $Ph(CH_2)_nCHO$ ($1 \leqslant n \leqslant 3$), the conversion of 4-phenylbutyraldehyde was monitored in order to examine in this type of reaction any systematics (table 1). Figure 3 illustrates that also this reaction gave the rearranged compound, butyrophenone, **5**, and formation of the α,β-unsaturated aldehyde 2-benzyl-6-phenyl-2-hexenal, **6**. All the tested catalysts show almost the

Table 1
The performance of phenylacetaldehyde, 3-phenylpropionaldehyde and 4-phenylbutyraldehyde on various CsLa-oxide and Cs-oxide supported catalysts

Catalyst	A_{wt} (mmol g^{-1} h^{-1})			Product selectivity [d] (%)					
	C_8H_8O [a]	C_9H_9O [b]	$C_{10}H_{10}O$ [c]	**1**	**2**	**3**	**4**	**5**	**6**
Cs/MCM-41	954	25.8	8.4	36.4	32.8	60.1	34.9	83.7	16.3
Cs/Na-MCM-41	736	24.4		46.4	12.8	67.8	15.0		
Cs/HMS	209	15.7	3.6	61.2	25.6	53.0	37.5	74.3	25.7
Cs/Na-HMS	101	12.8		59.3	19.6	24.2	35.6		
Cs/ASA1	600	16.3		15.1	44.2	68.4	23.2		
Cs/ASA2	3384	28.3		60.3	4.2	66.4	33.6		
Cs/Al_2O_3	1589	34.3		–	42.0	72.0	24.6		
CsLa/MCM-41	309	16.4	4.7	36.5	40.6	77.1	22.9	80.6	19.4
CsLa/Na-MCM-41	373	16.8	4.9	50.1	37.8	33.7	42.6	81.2	18.8
CsLa/HMS	719	23.5		65.9	37.8	60.3	35.0		
CsLa/Na-HMS	425	19.4		39.0	16.6	53.0	34.7		
CsLa/ASA1	250	11.1	7.3	11.1	78.4	57.3	42.7	83.7	16.3
CsLa/ASA2	702	23.8		31.3	23.6	78.5	21.5		
CsLa/Al_2O_3	1041	16.3		33.1	29.4	44.0	53.2		

[a] Specific activity at 30% phenyl acetaldehyde (C_8H_8O) conversion.
[b] Specific activity at 2 h 3-phenylpropionaldehyde (C_9H_9O) conversion.
[c] Specific activity at 2 h 4-phenylbutyraldehyde ($C_{10}H_{10}O$) conversion.
[d] The by-product is ethylbenzene and propylbenzene in the case of C_8H_8O and C_9H_9O, respectively.

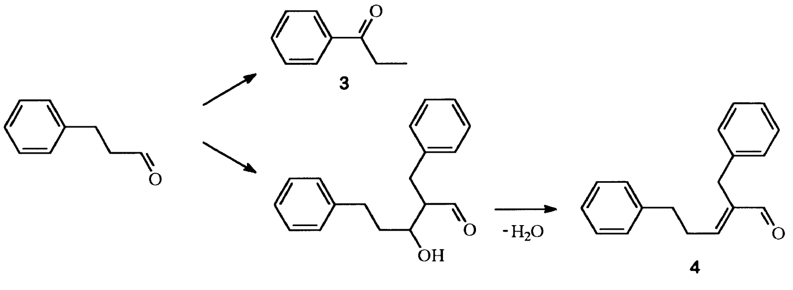

Figure 2. The reactions of 3-phenylpropionaldehyde over Cs and CsLa-oxide containing catalysts.

same product selectivity and no traces of butylbenzene could be detected.

Several related reactants were tested in order to elucidate the mechanism of this unknown reaction. First, phenylacetone did not rearrange to propiophenone, but remained unconverted at temperatures up to 170°C. When 2-phenylpropionaldehyde was subjected to the oxide catalysts only self-aldol condensation was observed leading to 1,5-diphenyl-3-hydroxy-2-methylpentanal. In case of an intramolecular aromatic substitution in the case of the phenylacetaldehyde to acetophenone rearrangement substituents at the phenyl group might have an effect on the product distribution and also on the rate of the reaction. It appeared that (3-methoxyphenyl)acetaldehyde was inactive whereas (4-methoxyphenyl)acetaldehyde gave exclusively 4-methoxyacetophenone **7** (figure 4). The performances of all the Cs- and CsLa-oxide containing catalysts were similar. The conversion of (4-methoxyphenyl)acetaldehyde, however, was lower than that of phenylacetaldehyde. Interestingly the conversion of (2-methoxyphenyl)acetaldehyde over the metal-oxide catalysts gives only the dehydrated-aldol product 2,4-di-(2-methoxyphenyl)-2-butenal and not the corresponding phenyl alkyl ketone. Formation of its substituted ethylbenzene compound was not observed.

When both ortho positions of phenylacetaldehyde contain a chloro substituent, again mainly aldol condensation takes place followed by dehydration giving 2,4-di-(2,6-dichlorophenyl)-2-butenal. Here the conversion was comparable with that of (4-methoxyphenyl)acetaldehyde.

3.2. Catalysts characterization

The X-ray diffraction patterns of the mesoporous aluminosilicates are in agreement with earlier reported data [7] and are therefore not depicted. It can be concluded that the structure of these materials is retained during preparation.

The strength and the amount of basic sites were analyzed by CO_2 temperature-programmed desorption (TPD). The number of basic sites is expressed by the metal atoms per CO_2-ratio of the catalysts, tabulated in table 2. In the ideal case this ratio should be 2 for Cs_2O and $CsLaO_2$ if the catalysts contain a perfect monolayer of metal oxide. The low ratios obtained for the studied catalysts indicate that the Cs- and CsLa-oxides show a good accessibility for CO_2 and are reasonably well homogeneously dispersed in a thin (2 layers averaged) layer of metal oxide. The basicity of a material is related by T_{max} and any desorption of CO_2 in the high temperature region would reflect strong basicity. As can be seen in figures 5 and 6, Cs/MCM-41 and Cs/HMS material show almost the same TPD plot of CO_2 in the low temperature as well as the higher temperature region. This indicates that Cs/MCM-41 and Cs/HMS are comparable in strength. Na^+ ion-exchange of HMS results eventually in a strong increase of the amount of basic sites but in a decrease in their strength. Cs/Na-MCM-41

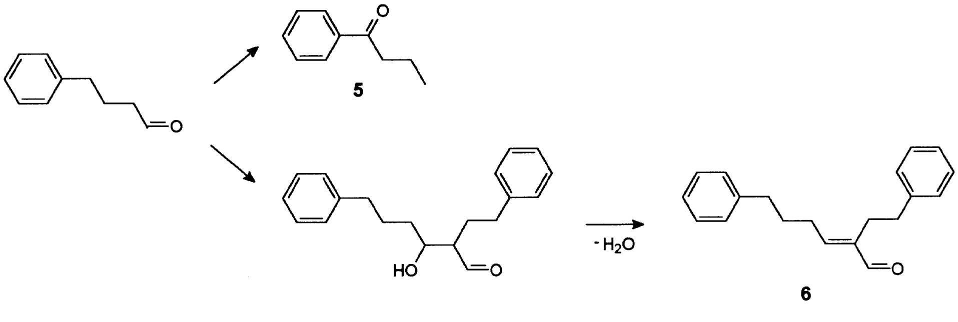

Figure 3. The reactions of 4-phenylbutyraldehyde over Cs and CsLa-oxide containing catalysts.

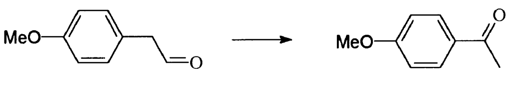

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Figure 4. The reaction of (4-methoxyphenyl)acetaldehyde over Cs and CsLa-oxide containing catalysts.

however, gave neither an improvement of the basicity nor of the amount of basic sites. Interestingly, Na^+ ion-exchange of the MCM-41 and HMS support reduces the width of the desorption-peak of the cesium oxide containing materials (figure 5). Ammonia TPD (table 2) shows for both Na^+ ion-exchanged mesoporous supports a decrease in the acidity. In contrast to Cs/Na-MCM-41 a clear reduction of the amount of acid sites is observed for the Cs/Na-HMS material. Figure 6 illustrates that the alumina and ASA2 supported cesium oxide systems, and to a lesser extent the ASA1 systems, are the strongest basic materials of the studied series which is reflected by the desorption in the high temperature region, though no distinct peaks are seen. Here the > 300°C area should be compared with the lines 3 and 4 in figure 5.

The amount of desorbed CO_2 for the CsLa-oxide containing materials is larger than that of the Cs-oxide materials which is caused by the occluded 5 wt% La metal. This is actually a matter of weight which is underlined by the calculated metal-to-CO_2 ratio which is comparable with these of the Cs-oxide containing materials. The basicity of the supported CsLa-oxides is somewhat lower than that of their Cs-oxide analogues which is reflected by a larger CO_2 desorption in the high temperature region. This was, however, not observed for the ASA1, ASA2 and alumina systems (figure 6). Na^+ ion-exchange of the MCM-41 and HMS support gave also for the CsLa-oxide containing materials a narrowing of the desorption peak. The amount of acid sites, measured by ammonia TPD, is in general higher than that of the La-omitted materials which is in agreement with the stronger Lewis acidic character of lanthanum.

Table 3 shows the specific surface area and the pore size of the mesoporous MCM-41 and HMS catalysts. Generally the HMS materials possess smaller mesopores than the MCM-41 materials which is in agreement with literature data [11,12]. The decrease in BET surface area for the metal oxide-loaded materials is caused by the presence of the intraporous Cs- and CsLa-oxide particles, giving only an increase in weight. The presence of these particles inside the pores is consistent with the decrease in the pore diameter, d_p [13].

4. Discussion

Aldol condensation of aldehydes over basic catalysts is a common reaction. That beside this reaction also rearrangement occurs of the aromatic aldehydes towards alkyl phenyl ketones is surprising. The presence of Cs in the catalysts is thereby probably a prerequisite. The reported aldol condensation of butyraldehyde over alkali oxide containing basic catalysts showed beside this also the Tishchenko reaction giving the dimeric ester [14]. The presence of acid sites at the surface of the catalyst is held responsible for this reaction. The Tishchenko reaction is generally catalyzed by Al Lewis

Table 2

CO_2 and NH_3 TPD data of various Cs and CsLa-containing catalysts

Catalyst	Desorbed CO_2 [a] (μmol/g)	Ratio [b] metal/CO_2	T_{max} [c] (°C)	Desorbed NH_3 [d] (μmol/g)	Ratio [e] metal/NH_3	T_{max} [f] (°C)
Cs/MCM-41	110	3.2	193	80	4.4	225
Cs/Na-MCM-41	70	4.3	188	100	3.0	189
Cs/HMS	90	3.8	210	150	2.2	184
Cs/Na-HMS	175	4.8	175	80	5.5	172
Cs/ASA1	90	3.6	203	120	3.1	154
Cs/ASA2	12	3.1	202	570	0.6	132
Cs/Al_2O_3	15	2.5	203	110	3.4	246
CsLa/MCM-41	190	3.7	166	540	0.8	170
CsLa/Na-MCM-41	160	4.9	163	330	2.3	169
CsLa/HMS	190	3.5	205	1001	0.7	197
CsLa/Na-HMS	170	4.2	184	180	0.2	197
CsLa/ASA1	160	4.5	202	150	5.6	225
CsLa/ASA2	190	3.1	203	730	0.8	178
CsLa/Al_2O_3	220	2.8	174	310	2.0	202

[a] Amount of desorbed CO_2 measured by TPD.
[b] The number of metal atoms per the number of CO_2 molecules.
[c] Temperature corresponding to the maximum of the CO_2 TPD plot.
[d] Amount of desorbed NH_3 measured by TPD.
[e] The number of metal atoms per the number of NH_3 molecules.
[f] Temperature corresponding to the maximum of the NH_3 TPD plot.

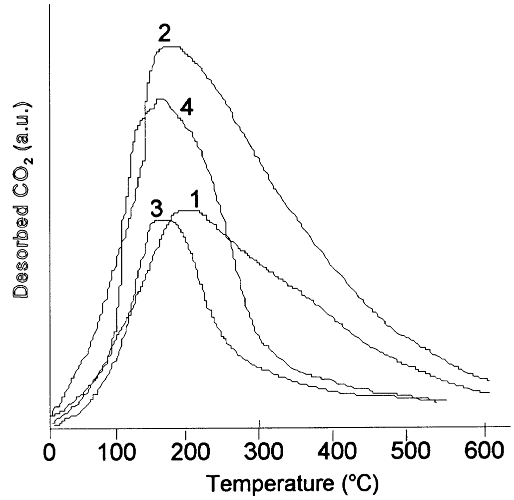

Figure 5. TPD plots of CO_2 on Cs/MCM-41 (1), CsLa/MCM-41 (2), Cs/Na-MCM-41 (3) and CsLa/Na-MCM-41 (4).

centers (e.g. $AlOEt_3$). The authors [14] reported also that the sodium-, potassium- and rubidium oxide-loaded alumina are very active basic catalysts in the self-condensation of butyraldehyde at 50°C giving 2-ethyl-3-hydroxyhexanal, its corresponding dehydrated product and the trimeric glycol ester, a Tishchenko-type cross esterification product. The alkali oxide-loaded zeolite X catalysts required, however, a significantly longer reaction time to achieve the same conversion.

The isomerization of phenylacetaldehyde to acetophenone can, in accordance with the work of other researchers, at first sight be explained by a phenyl-shift [1,2]. This mechanism can, however, not explain the rearrangement of 3-phenylpropionaldehyde and 4-phenylbutyraldehyde to propiophenone and butyrophenone, respectively. Moreover, in this case basic catalysts are used instead of mildly Brønsted and Lewis acidic zeolites like B-MFI and Fe-MFI [1,2]. Therefore a general mechanism has to be proposed in which the reaction is base catalyzed which results eventually in the rearrangement of the aryl alkyl aldehyde into the corresponding phenyl alkyl ketone.

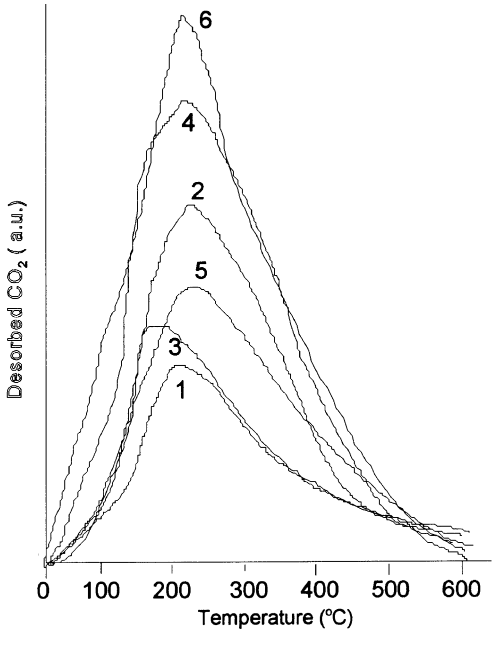

Figure 6. TPD plots of CO_2 on Cs/ASA1 (1), CsLa/ASA1 (2), Cs/ASA2 (3), CsLa/ASA2 (4), Cs/Al_2O_3 (5) and CsLa/Al_2O_3 (6).

Table 3
Nitrogen physisorption data of Cs and CsLa-containing MCM-41 and HMS materials

Sample	BET area (m^2/g)	d_p [a] (Å)
MCM-41	758	36
Cs/MCM-41	700	29
CsLa/MCM-41	660	35
HMS	1100	29
Cs/HMS	1040	26
CsLa/HMS	860	26

[a] Corrected pore diameter d_p according to Broekhoff and De Boer [13].

When accepting a basic mechanism the first step in the rearrangement is probably abstraction of the α-proton giving a carbanion. Bond breaking between the carbonyl carbon and the α-carbon as the second step is not very obvious, though, other researchers have used this mechanism to explain the product formation in the base-catalyzed aldol condensation of acetone [15]. Bond breaking is also proposed in the photo-rearrangement of aromatic ketones over alkali ion-exchanged zeolites but here radical formation is involved [16,17].

Considering the type of products formed it is plausible to propose a mechanism in which the carbonyl group attacks the phenyl ring via a cyclic intermediate. The 1- and 2-position of the ring are candidates to play a role in this process. The exclusive formation of 4-methoxyacetophenone from (4-methoxyphenyl)acetaldehyde, the inactivity of (3-methoxyphenyl)acetaldehyde and the aldolization of (2-methoxyphenyl)acetaldehyde favours the idea that the rearrangement involves a nucleophilic attack at the 1-position of the phenyl group. In general methoxy-substituents have an activating ability at the corresponding ortho and para positions for aromatic electrophilic substitution. As to nucleophilic substitution the reverse is expected to hold. The lower rate of the reaction of (4-methoxyphenyl)acetaldehyde is therefore in agreement with the deactivating power of the *p*-methoxy-substituent for nucleophilic substitutions. The virtual inactivity of (3-methoxyphenyl)acetaldehyde remains to be explained, though it is not in contradiction with the proposed mechanism.

It is plausible that the methoxy-substituent at the *o*-position hinders the (nucleophilic) attack giving a three-

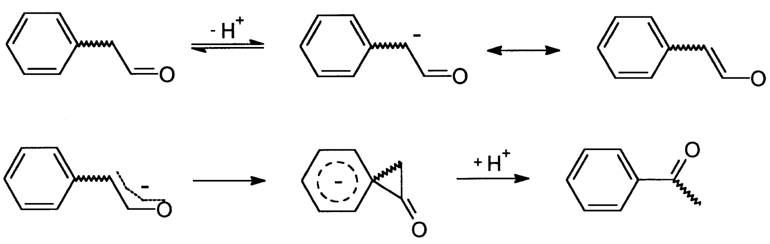

Figure 7. General mechanism for the rearrangement of an ω-phenylalkanal to a phenyl alkyl ketone.

membered ring intermediate (figure 7). Aldol condensation is therefore the most reasonable option in this reaction system. When both ortho positions are occupied by chloro atoms again aldolization followed by dehydration is observed. It should be mentioned that the ring-type intermediate for 3-phenylpropionaldehyde and 4-phenylbutyraldehyde is four- and five-membered, respectively. Figure 7 illustrates such ring-type intermediates by changing the corrugated bond by two or three bonds, respectively.

As visualized in figure 8 the presence of Cs^+ cations in all the catalysts can lower the electron density of the phenyl group by π-coordination [18–20]. This interaction stimulates the nucleophilic substitution at the phenylic ring. Interaction of the carbonyl-oxygen with Cs^+ or La^{3+} ions results in an increase in the acidity of the α-proton which is therefore activated for abstraction by the negative charged oxygen ions of the metal oxide. Interaction of toluene and formaldehyde with Lewis acidic Cs^+ ions and basic oxygen sites in Cs^+ ion-exchanged or cesium oxide loaded zeolites has been proposed in the side-chain alkylation of toluene [18,19]. Quantumchemical studies demonstrate that interactions of carbonyl-oxygens with Lewis acid alkali cations lead to a transfer of electron density from the carbonyl compound to the alkali containing zeolite [19,21]. This results in a weakening of the α-C–H bonds. Comparable results are achieved by infrared studies on ketone loaded zeolites [22]. The Lewis acid sites in the Cs- and CsLa-oxide containing materials are also held responsible for the dehydration of the aldol products giving the α,β-unsaturated aldehydes.

Strongly basic sites present in cesium oxide loaded MCM-41 and HMS materials are effective for the rearrangement and aldol condensation. In general the HMS systems produce more of the phenyl alkyl ketone than the larger-sized α,β-unsaturated aldehyde. Considering the equal basicity the higher affinity in producing the smaller molecule is probably caused by the smaller mesopores of HMS compared to those of MCM-41. The lower activity of Cs/HMS in the other reactions in which even larger molecules are involved, may also result from the smaller pores of the catalyst. In contrast to the very high activity of the strongly basic alumina and ASA2 systems in the conversion of phenylacetaldehyde these systems show activities comparable with the MCM-41 and HMS catalysts in the conversion of 3-phenylpropionaldehyde and 4-phenylbutyraldehyde. This is tentatively assigned to the large size of the molecules and the corresponding products. Beside the fact that Cs/ASA2 and Cs/Al_2O_3 are strongly basic and very active catalysts, at least in the conversion of phenylacetaldehyde, they both produce substantial amounts (up to 50%) of ethylbenzene. This reduction product requires at least a hydrogen source. Although it is very speculative, it is possible that the hydrogen-shift depicted in figure 7 is a very slow step and is therefore in competition with the reduction of phenylacetaldehyde. Further investigations are required to get more insight in this side-reaction.

The Na^+ extraframework ions in the mixed cations systems studied show no enhanced effect on either the activity or basicity. A weaker interaction of the oxides adjacent to the aluminum of the support might be a result. Considering the supported CsLa-oxide materials it can be noticed that, in spite of their lower basicity [7], these systems are quite active and selective to the phenyl alkyl ketones. The reason for this is that lanthanum activates the α-proton via coordination of the carbonyl oxygen. It is noteworthy that the Tishchenko reaction is not observed over the Lewis acidic lanthanum containing catalysts and the other materials. It has been reported that the alkali oxide-loaded alumina and zeolite X produce a significant amount of the trimeric glycol ester, a product from the Tishchenko reaction of butyraldehyde and its aldol dimer [14].

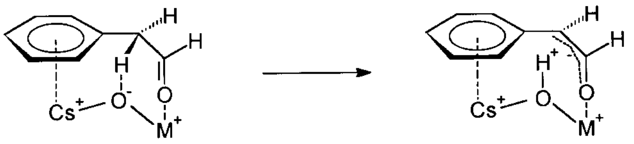

Figure 8. Schematic presentation of the interaction of phenylacetaldehyde with cesium oxide and cesium–lanthanum oxide (M = Cs and La, respectively). The oxygen and metal ions are the basic and acid sites, respectively.

5. Conclusions

Aluminosilicate MCM-41 and HMS, amorphous silica–alumina and alumina containing Cs and CsLa-oxide are effective catalysts for the rearrangement of ω-phenylalkanals to phenyl alkyl ketones in the liquid phase. The mechanism of this hitherto unknown isomerization is proposed to go via an intramolecular aromatic nucleophilic substitution at the 1-position involving a cyclic transition state. The presence of cesium ions is playing probably a key role in this process. The product ratio can be influenced by factors like the basicity of the catalyst and the size of the mesopores.

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