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Aldol Condensation of Furfural and Acetone on Layered Double Hydroxides[1]

Huihui Liu, Wenjie Xu, Xiaohui Liu, Yun Guo, Yanglong Guo, Guanzhong Lu, and Yanqin Wang

Lab for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, People's Republic of China

e-mail: wangyanqin@ecust.edu.cn, xhliu@ecust.edu.cn

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Abstract—The Aldol condensation of furfural (Fur) with acetone (Ac) to 4-(2-Furyl)-3-buten-2-one (FAc) is one of the most important processes in the aqueous-reforming of oxygen-containing bio-mass derivatives and has been carried out in the presence of solid-base catalysts, calcined-rehydrated Layered Double Hydroxides (LDH). The Mg–Al Layered Double Hydroxides has been prepared by the co-precipitation, calcination and regeneration from mixed oxides by rehydration. The catalyst prepared with different Mg/Al molar ratios showed different catalytic performance and the best catalyst was with the Mg/Al molar ratio of 2.5. Phenol adsorption showed that the best catalyst had the largest numbers of accessible basic sites. The appropriate rehydration temperature and time for mixed oxides obtained by calcination were also investigated. The Mg–Al LDH catalysts can be regenerated by calcination at 773 K and rehydration in de-carbonate water, but the regeneration is complex and incomplete. In addition, the catalyst calcined at high temperature also had activity, which was attributed to the formation of the Mg–Al spinels.

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1. INTRODUCTION

People are now suffering from the pressures of both economic growth and environmental protection. It's important to protect, exploit and use energy sources. Renewable resources has been exploited and used all over the world considering the advantages of environmental protection, increasing employment and energy sources safety. Among these renewable resources, biomass energy is an important energy and it is the fourth energy besides coal, petroleum and natural gas and has a high position in energy system. Furfural, which is available from the renewable farm and forest plant in industry, can be used as a starting material for the C_8 alkane by the Aldol condensation of furfural and acetone, and further by the hydrogenation and dehydration; and for the C_{13} alkane by the Aldol condensation of C_8 and furfural with the similar processes [1]. The two alkanes can be used as renewable resources.

Aldol condensation plays an important role in the aforementioned process. Normally, this kind of reaction is practiced industrially by using homogenous base catalysts, such as sodium and calcium hydroxide. However, these processes would generate significant water streams that must be neutralized and leads to an additional disposal cost. Developing a new active and stable solid base catalyst can simplify the process, promote clean manufacturing, and decrease the production cost. Among the solid base catalysts, activated hydrotalcite-like compounds (HTLCs) or Layered Double Hydroxides (LDHs) have been found to be the promising candidates of aldolization catalysts [2–5]. Layered Double Hydroxides (LDHs) known as anionic clays, are natural or synthetic materials consisting of the positively charged brucite-like sheets with the general formula of

$$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n} \cdot yH_2O,$$

where M^{2+} and M^{3+} represent divalent and trivalent cations in the octahedral sites within the hydroxyl layers, x is equal to the ratio of $M^{3+}/(M^{2+} + M^{3+})$ with a value varying in the range of 0.17–0.50, and A is an exchangeable interlayer anion [6–8], Carbonates are the interlayer anions in naturally occurring hydrotalcites. However, the number of counterbalancing ions is essentially unlimited, and LDHs intercalated by various simple inorganic, polyoxometalate, and complex as well as organic anions have been synthesized.

The Mg–Al LDHs can be used as catalyst both in the form of Mg(Al)O mixed oxides obtained by the calcination of an Mg/Al hydrotalcite precursor and the rehydrated form of these calcined materials [9]. The rehydrated hydrotalcites possess Brønsted basic sites and in most studies these catalysts are more active and selective to the across-condensation products than the mixed oxides [10–15]. Roelofs et al. [13, 16] demonstrated that less than 5% of the total number of OH^- in the rehydrated samples was available for the condensation reactions and the activity was attributed to the localized OH^- at the edge of the reconstructed platelets of the layered structures. While, Climent et al.

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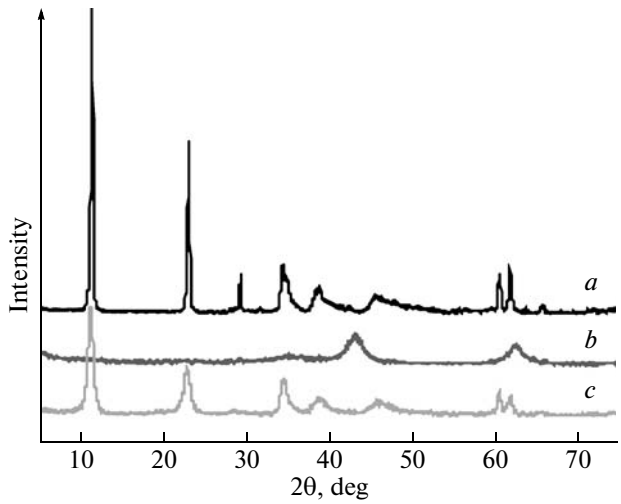

Fig. 1. XRD patterns of *a*, C-LDH; *b*, C-LDO; and *c*, C-RLDH (Mg/Al = 2.5).

[11] suggested that the OH^- sites in the rehydrated samples are of medium basic strength and thus well adapted to the Aldol condensation.

In this paper, Layered Double Hydroxides (LDHs) were prepared by co-precipitation and characterized by XRD, FT-IR and BET. The condensation of furfural and acetone was carried out in the presence of activated MgAl–LDHs and the influence of the preparation method; Mg/Al molar ratios; rehydration temperature and time on the catalysis properties were investigated.

2. EXPERIMENTAL

2.1. Preparation of the Catalyst Precursor

The LDH samples were prepared by co-precipitation from an aqueous solution of magnesium and aluminum nitrate (solution A) and a highly basic carbonate solution (solution B). Solution A, containing $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was 0.6 M (Al + Mg) with an Mg/Al molar ratio equal to 2, 2.5, or 3. Solution B was prepared by dissolving appropriate amounts of Na_2CO_3 and NaOH in distilled water in order to obtain 0.1 M [CO_3^{2-}] and 1.2 M [OH^-].

In the synthesis procedure, solution B was placed in a 500 ml PTPE reactor and solution A was slowly dropped into it with vigorous stirring at a constant temperature of 313 K. After that, the gel was stirred at 363 K for 24 h. Then the solid was obtained after filtered, washed with distilled water and dried at 373 K for 24 h. The as-synthesized Layered Double Hydroxides by this way was denominated as C-LDH, with CO_3^{2-} as the counterions in the interlayer.

2.2. Catalyst Activation

The MgAl-mixed oxides (C-LDO) were obtained by calcination of C-LDH at 673 K for 4 h in the air with a heating rate of 5 K min^{-1}. The mixed oxides were rehydrated in de-carbonated water at a given temperature for several hours. Then the activated catalysts were obtained by drying under vacuum at 373 K and denominated as C-RLDH, but with OH^- ions as the counterions in the interlayer.

2.3. Characterization

XRD powder patterns were collected on a Rigaku D/Max 2550VB/PC instrument using monochromatized Cu-$K_{\alpha 1}$ radiation (λ = 0.154056 nm, 40 kV, and 100 mA) and IR spectra were recorded with a Nicolet Nexus 670 spectrophotometer.

The adsorption of phenol was used to characterize the available basic sites of the solid base. The experiment was carried out in cyclohexane at 298 K and the amount of phenol adsorbed by the solids was measured by UV-Vis spectroscopy (λ_{max} = 271.6 nm) [17, 18].

Nitrogen adsorption and desorption isotherms were measured at 77 K with a Micromeritics ASAP2020M sorption analyzer. Before the measurements, the samples were outgassed at 373 K for 8 h.

2.4. Catalytic Activity Measurement

The catalytic tests were performed in a sealed bottle. 0.5 g catalyst was added to a mixture of 14.5 g acetone and 2.4 g furfural and kept at 373 K for 10 h. After reaction, the liquid was taken from the reaction mixture and analyzed by a PerkinElmer Clarus 500 gas chromatography with a SE-54 column. A flame ionization detector (FID) was used to analyze the final products, and an internal standard quantitative analysis method was used.

In the condensation of furfural and acetone, FAc was the major and aim reaction, product. Because of the symmetry of acetone molecule, a further condensation with furfural will happen, which led to the formation of 1,4-pentadien-3-one, 1,5-di-2-furanyl (F_2Ac), as a minor product. The Aldol condensation of acetone itself can occur, but the corresponding product was not found in our analysis by GC because of the thermodynamic limitation.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Catalysts

The catalyst precursor was synthesized by co-precipitation with an Mg/Al molar ratio of 2.5. After calcination and rehydration, the activated catalyst was obtained. The XRD patterns of the as-prepared precursor, C-LDH (a); calcined mixed oxide, C-LDO (b) and rehydrated, active catalyst, C-RLDH (c) were presented in Fig. 1. The XRD pattern of the as-pre-

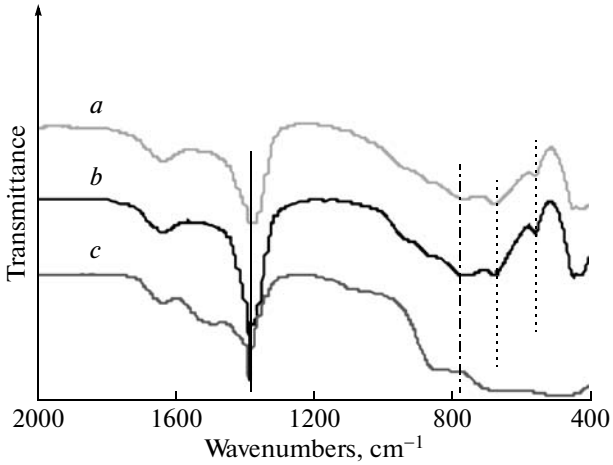

Fig. 2. FI-IR spectra of (*a*) C-LDH, (*b*) C-LDO, and (*c*) C-RLDH (Mg/Al = 2.5).

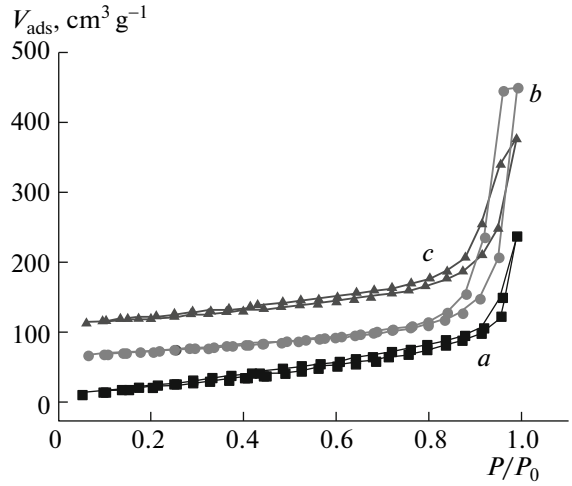

Fig. 3. N_2 adsorption-desorption isotherms of the different samples: (*a*) C-LDH, (*b*) C-LDO, and (*c*) C-RLDH.

pared LDH (Fig. 1*a*) showed well-defined sharp and symmetric peaks for (003), (006), (110) and (113) planes, as well as broad symmetric peaks for the (009), (015), and (016) planes. These peaks were characteristic reflections of clay minerals with layered structure [19]. The sharp peaks showed that the well-crystallized hydrotalcites were formed. After calcination, all these characteristic peaks of the layered structure were disappeared in the XRD pattern of the MgAl-mixed oxides (Fig. 1*b*), which meant that the layered structure was collapsed. The peaks in Fig. 1*b* were characteristic reflections of MgO. In the XRD pattern of the rehydrated sample (Fig. 1*c*), these characteristic peaks of the layered structure were reappeared, which showed that the layered structure was returned. Due to the memory effect of hydrotalcites, the rehydration of Mg-Al mixed oxides led to the layered structure's reconstruction.

The FT-IR spectra of C-LDH (*a*), C-LDO (*b*), and C-RLDH (*c*) were presented in Fig. 2. In Fig. 2*a*, the peak at 1360 cm^{-1} was attributed to the vibration of CO_3^{2-} existed in the interlayer of LDH. In Fig. 2*b*, the peak at 1360 cm^{-1} was changed and shifted to 1388 cm^{-1} with much weaker strength. This meant that CO_3^{2-} was almost eliminated by calcination, but not completely. In Fig. 2*c*, the vibration peak of CO_3^{2-} reappeared at 1360 cm^{-1}, which meant that a little amount of CO_3^{2-} still existed during the process of calcination and rehydration. In low spectrum band, the peak around 555 cm^{-1} was attributed to the shifting vibration of Al–OH or Mg–OH. The peak at 687 cm^{-1} was attributed to the bending vibration of Al–OH or Mg–OH, and the peak at 787 cm^{-1} was attributed to the stretching vibration of Al–OH or Mg–OH. All these peaks were disappeared in the MgAl-mixed oxides (Fig. 2*b*), which showed that the calcination led to the collapse of the layered structure. But in the pattern of the rehydrated sample (Fig. 2*c*), these peaks reappeared, which showed that the layered structure was reconstructed with OH^- mostly replaced CO_3^{2-} in the interlayer. These results are accorded with the previous reports [20–22].

Figure 3 showed the N_2 adsorption–desorption isotherms of the three samples. Upon calcination, the porosity is increased in C-LDO, in accordance with the increase in BET surface area from 35 to 123 m^2 g^{-1} (Table 1). Such behavior has been reported for LDH containing carbonates and assigned to the formation of craters through the layers due to evolution of CO_2 and H_2O [23]. Rehydration of C-LDO in the liquid phase by stirring produced an increase in surface area due to the rupture of particles and a marked exfoliation of the crystals.

3.2. Aldol Condensation of Furfural and Acetone

3.2.1. Influence of the Mg/Al molar ratio. Due to the particularity of MgAl-LDH, the ratio of Mg/Al determined the structure of LDH. For lower Mg/Al ratio, the increase in the number of neighboring Al-containing octahedral led to the formation of $Al(OH)_3$, whereas high Mg/Al ratio led to the segregation of $Mg(OH)_2$ due to the high density of Mg-containing octahedral in the Brucite-like sheets [24]. Pure

Table 1. Structural properties of the samples

Samples	Phase	S_{BET}, m^2 g^{-1}	Pore volume, cm^3 g^{-1}
C-LDH	Periclase	35	0.37
C-LDO	Meixnerite	123	0.62
C-RLDH	Meixnerite	133	0.53

Table 2. Reaction results of the catalysts with different Mg/Al molar ratio

Mg/Al	Conversion of Fur, %	Selectivity to FAc, %	Yield of FAc, %
2 : 1	62.4	67.3	41.3
2.5 : 1	78.6	72.3	56.9
3 : 1	66.4	55.2	36.6

Table 3. Reaction results of the catalysts at different rehydration temperature (Mg/Al = 2.5)

Temperature, K	Conversion of Fur, %	Selectivity to FAc, %	Yield of FAc, %
323	74.6	50.8	37.9
333	73.2	59.2	43.3
343	78.6	72.3	56.9
363	74.9	75.4	56.5

hydrotalcites with high crystallinity could be prepared at Mg/Al ratios between 2 and 4 [25, 26]. So, three samples with different Mg/Al ratio were prepared to investigate the influence of Mg/Al ratio on the catalytic activity (Table 2).

It can be seen from Table 2 that the catalyst with Mg/Al ratio equal to 2.5 showed the best catalytic activity with furfural conversion reaching to 78.6% and the selectivity to FAc being 72.3%. From XRD analysis, the three catalysts all have the layered structure (Fig. 4), so the difference of the activity and selectivity to FAc was not come from the crystal structure, but may be attributed to the numbers of surface basic sites and strengths. The numbers of the accessible basic sites of these catalysts were measured by phenol absorption and presented in Fig. 5.

Figure 5 showed that all the three catalysts could absorb phenol, which meant that they all owned surface basic sites, and C-RLDH with Mg/Al = 2.5 has the most basic sites, which accordance with its best catalytic activity. In addition, we noted that the selectivity to FAc increased as the amount of base site on the surface of material increased. The reason for rehydrated catalyst with Mg/Al = 2.5 owned the most basic sites could be explained as follows: on the one hand, the Al content decreased with increasing the Mg/Al molar ratio from 2 to 2.5, which led to the numbers of the positive charge on layer decreased. Accordingly, the number of OH^- formed from aqueous solution in interlayer counterpoised the positive charge on layer was decreased, which brought the decrease of the accessible basic sites. On the other hand, as Mg/Al was close to 3, steady layered structure for LDH was easily formed, because the Mg/Al of natural hydrotalcite was equal to 3. And OH^- could be arranged in order on steady structure, which led to high density of basic sites. The two factors were contradicted, which led to the catalyst with Mg/Al = 2.5 had the most basic sites relative to 2 and 3.

3.2.2. Influence of the rehydration temperature and time. Catalysts rehydrated at different temperatures were prepared and their catalytic performance was listed in Table 3.

All the rehydration time were fixed at 2 h. Table 3 showed that the selectivity and yield to FAc increased with the rehydration temperature from 323 to 343 K, but the further increase of the rehydration temperature from 343 to 363 K didn't change the selectivity and yield greatly.

When fixed the rehydration temperature (343 K) and prolonged the rehydration time, the catalytic activity also changed, but not too much. The results were presented in Table 4.

From Table 4, the catalyst with longer rehydration time didn't showed better catalytic performance. So

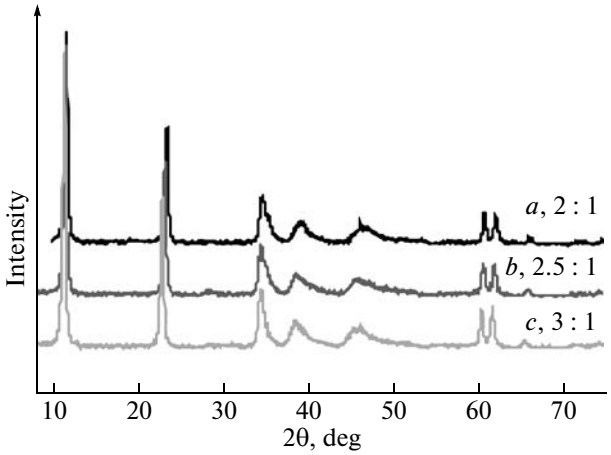

Fig. 4. XRD patterns of the three different samples: (*a*) C-LDH, (*b*) C-LDO, and (*c*) C-RLDH.

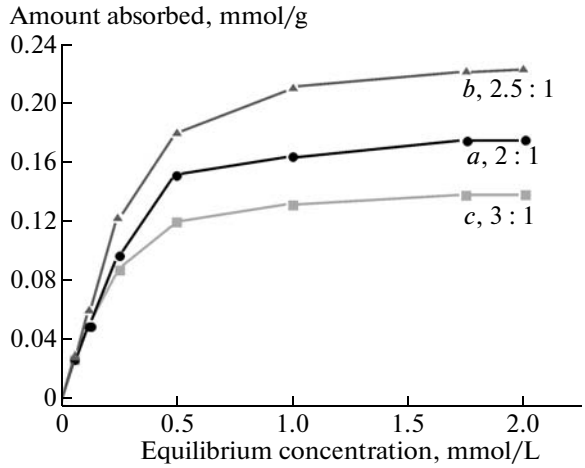

Fig. 5. The adsorption of phenol from cyclohexane on different catalysts: (*a*) C-LDH, (*b*) C-LDO, and (*c*) C-RLDH.

we believed the appropriate rehydration temperature and time for Mg–Al mixed oxides were 343 K and 2 h, respectively.

3.2.3. Reutilization and regeneration. For solid base catalyst, its reusability and regeneration was important. The reusability was conducted over a used catalyst from a typical experiment after cooling down the reactor to room temperature, recovery of the solid by washing with acetone, and drying under vacuum at 373 K for 1 h. Showed that the furfural conversion over the catalyst after one run was much lower than that on the fresh catalyst (45% vs. 73%). The deactivation of the catalyst may be due to the adsorption of the reaction products (polyunsaturated molecules such as FAc) or products derived from furfural oligomerization during the reaction. Because the catalyst after one run was deeply brown, while the fresh was white. These deposits maybe prevent the accessibility of the active OH^- centers, and than lead to lower conversation. Importantly, the selectivity to FAc was remained constant (77%), which indicated that these deposits did not modify the nature of the active OH^- centers.

The regenerated LDH was obtained by calcined the used catalyst at 773 K for 4 h in air in order to remove the carbonaceous deposits, followed by rehydration in decarbonated water at 343 K. The conversion of furfural was slightly recovered, but still lower than that of the fresh one (55% vs. 73%), but the selectivity to FAc was largely increased to 97%. Furthermore, the regenerated catalyst was slightly yellow, which showed that the calcination temperature was not sufficient to completely eliminate the carbonaceous deposits. But 773 K was the allowed highest temperature, because the layered structures can not be reconstructed when the calcination temperature was above 773 K. Therefore, the regeneration of the LDH was not complete, which explained the lower furfural conversion. It can be proposed that the regeneration process reduce the number of active sites in the sample, rendering lower catalytic activity, and affect the quality of the regenerated centers, as the FAc selectivity is increased; the latter is still under consideration.

3.2.4. Calcination with high temperature. MgAl–CO_3^{2-} LDHs treated by calcination below 773 K and rehydration could turn into MgAl–OH^--LDHs with the same structure, which could catalyze the condensation of furfural with acetone, but the recovery of the catalyst is complex and incomplete. When the calcination temperature was higher than 773 K, it would convert to mixed oxides with basicity. So we calcined MgAl–CO_3^{2-}-LDHs at different temperatures higher than 873 K, and used the mixed oxides as catalysts directly.

As shown in Table 5, for mixed oxides calcined at 873 K, the conversion of furfural and the selectivity to FAc were very low. When the calcination temperature was increased to 973 K, the conversion of furfural and the selectivity to FAc were enhanced greatly. Further increase the calcination temperature, the conversion of furfural was increased slowly, but the selectivity to FAc reached maximum at 1073 K, than decreased a little bit at 1173 K. To explain this, their structures were analysized by XRD measurement (Fig. 6). After calcination at 873 K, MgO was formed as shown in Fig. 6*a* and MgO had strong basicity as it was known, but a Lewis alkali, different from MgAl–OH^--LDHs, which is a Brønsted alkali. According to the previous work [9], Lewis alkali was not an effective catalyst for the cross-condensation, so it is explained why the mixed oxides calcined at 873 K had weak catalytic performance. When the calcination temperature reached 973 K, the structure was a bit different from that calcined at 873 K, because the new peaks appeared around 32° and 59° in pattern *b*, which is corre-

Table 4. Reaction results of catalysts of different rehydration time (Mg/Al = 2.5)

τ, h	Conversion of Fur, %	Selectivity to FAc, %	Yield of FAc, %
2	78.6	72.3	56.9
3	84.1	66.3	55.8
4	80.2	68.9	55.3

Table 5. Catalytic performance of the catalyst with high calcination temperatures (Mg/Al = 2.5)

Temperature, K	Conversion of Fur, %	Selectivity to FAc, %	Yield of FAc, %
873	18.6	30.4	5.7
973	61.4	63.3	38.9
1073	80.3	64.9	52.1
1173	84.6	60.4	51.1

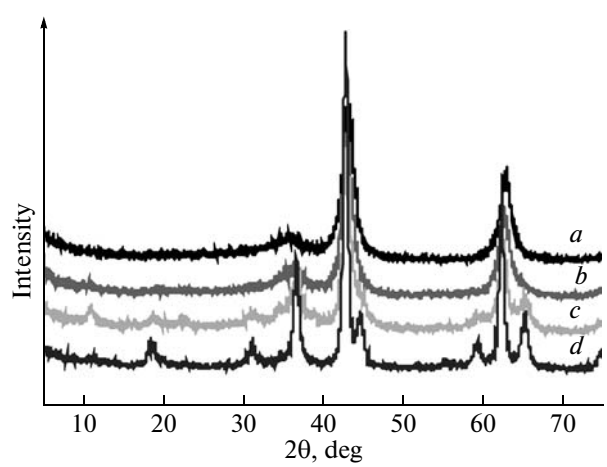

Fig. 6. XRD patterns of the samples calcined at (*a*) 873, (*b*) 973, (*c*) 1073, and (*d*) 1173 K.

sponded to the spinel-type structure. When LDH was calcined at 1073 K, the peaks indexed to spinel phase appeared, and the catalytic activity got to the maximum. Further increase of the calcination temperature led to the sharpening of the XRD pattern, indicating the well crystallization of the spinel phase, while the conversion and selectivity changed a little bit. All the above analysis presented that MgAl-spinel could be used as catalyst for the condensation of furfural with acetone.

4. CONCLUSIONS

MgAl—LDHs have been synthesized by co-precipitation. Both XRD patterns and FT-IR spectra showed that MgAl–LDHs with the layered structures turned into MgAl-mixed oxides by calcination with the layered structures collapsed, and recovered by the rehydration of mixed oxides with the reconstruction of the layered structure. Thus reconstructed LDHs can be used as the solid base catalyst in the Aldol condensation of furfural and acetone.

The catalyst with different Mg/Al molar ratios showed different catalytic activities with the same structure. The highest furfural conversion and FAc selectivity were obtained with the Mg/Al molar ratio of 2.5, which had the most surface basic sites. The appropriate rehydration temperature and time for mixed oxides obtained by calcination were also investigated and found that 343 K was appropriate rehydration temperature and 2 h was a suitable rehydration time. The reutilization and regeneration of the solid catalyst were also investigated, but the regeneration is complex and incomplete. In addition, the catalyst calcined at high temperature also had activity, which was attributed to the formation of the Mg–Al spinels. A new kind of spinel type solid catalyst can be synthesized at lower temperature and easy to be regenerated is being under study because Mg–Al LDHs are hard to be regenerated.

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