



Short communication

Low cost and non-surfactant synthesis of fluorinated alumina modified with magnesium for condensation of aniline to diphenylamine

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ABSTRACT

Fluorinated alumina was modified with different alkaline and alkaline earth metals. And fluorinated alumina modified with magnesium was found to show the best reactivity and selectivity for condensation of aniline to diphenylamine (DPA) under fix-bed continuous flow reaction conditions. Various characterizations involving X-ray diffraction, nitrogen-adsorption measurements, inductive coupled plasma emission spectrum as well as infrared spectrum has integrally testified the structure of fluorinated alumina modified with magnesium. The preparation of fluorinated alumina modified with magnesium was simply convenient and, importantly, environmentally benign for non-surfactant needed in comparison with H-beta zeolite. Meanwhile, the catalyst even exhibited higher conversion of aniline than H-beta zeolite. Such alumina-based catalyst can be readily recovered for at least 5 times, while the conversion of aniline and productivity for DPA was almost maintained during the reaction.

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1. Introduction

Diphenylamine (DPA) is an important chemical additive for the synthesis of rubber chemicals, dyes, and stabilizer for polymers, etc. [1]. Among all the preparation methods for DPA, condensation of aniline in the presence of H-beta zeolite as solid acid catalyst was most widely implemented on relatively large scales [2,3]. Ordinarily, H-beta zeolite is synthesized with organic surfactant, such as tetraethyl ammonium hydroxide, in strict hydrothermal conditions [4]. Hence, the synthesis processes are often complicated, costly and environmentally unfriendly [5,6].

A cleaner process for solid acid without by-products is of great significance for the economical preparation and industrial application of acid catalysis [7]. The same sustainable approaches to the production of DPA have also stimulated the use of eco-friendly, highly active heterogeneous catalysts as alternatives [8,9]. Any solid acid catalyst, as effective as H-beta zeolite in condensation of aniline, are potentially applicable for the efficient conversion of aniline, and the preparation of the catalysts should be easy, non-corrosive and non-synthetic organic surfactant to be needed, allowing for regeneration of the catalyst with low energy consumption [10–12]. The catalytic performance for condensation of aniline to DPA depends not only on the structure of the

individual solid catalysts but also on the number of their active sites and the corresponding acid strength [1,13]. In this work, we first developed and prepared fluorinated alumina modified with magnesium via a simple method instead of surfactant-assisted hydrothermal synthesis of H-beta zeolite for production of DPA. The fluorinated alumina is a solid acid catalyst consisting of rich Brønsted and Lewis acid sites with three dimensional mesoporous networks and it was readily prepared by fluorination of the certain alumina with a high surface area and pore volume [14,15]. Such fluorinated alumina modified with magnesium catalysts are rare to date. This incorporation provides simple and eco-friendly access by reactants in condensation of aniline, which gives rise to unexpected high catalytic performance for acid reaction in comparison with H-beta zeolite.

2. Results and discussion

2.1. Catalyst characterization

For the catalytic performance of the individual catalysts depends on the structure of the solid [1], the powder XRD characterization of fluorinated alumina modified magnesium with different fluorine content was analyzed. Their diffraction patterns are given in Fig. 1. Detailed meaning of abbreviations for different catalysts could be seen in Section 4.1. From Fig. 1; effective modification of alumina with fluorine could be observed. The diffraction patterns of the catalysts were similar to pure alumina

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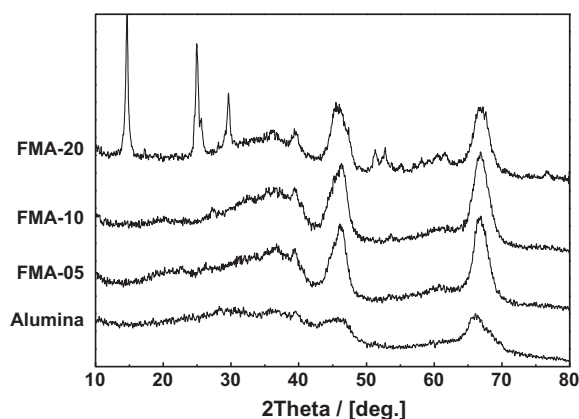


Fig. 1. X-ray diffraction pattern of different fluorine content (ammonium fluoride) fluorinated alumina modified with magnesium.

sample except for high fluorine content of FMA-20. The typical diffraction peaks of the γ - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ could be observed ($2\theta = 14.7^\circ$; 25.0° and 29.7°) [10]; and the signals of catalyst pattern with high fluorine content ($2\theta = 31.5^\circ$ and 52.8°) assigned to $\text{AlF}_{1.65}(\text{OH})_{1.35} \cdot n\text{H}_2\text{O}$ [16]; meanwhile, small additional peaks ($2\theta = 17.2^\circ$ and 62.0°) are identical with the typical pattern of $(\text{NH}_4)_3\text{AlF}_6$ [14]. When catalysts with fluorine content lower than 13 wt%; the XRD technique does not allow to get any information [17]. There are two kinds of explanation for the fluorination mechanism of alumina by NH_4F . One is the formation of $(\text{NH}_4)_3\text{AlF}_6$ over fluorinated alumina by the following reaction:



$(\text{NH}_4)_3\text{AlF}_6$ transformed into $(\text{NH}_4)_4\text{AlF}_4$, γ - AlF_3 and finally α - AlF_3 respectively at 573, 773 and 873 K [18]. However, the other mechanism also raised that the formation of AlF_3 by NH_4F to be the result of consecutive reactions between $\text{Al}(\text{OH})_3$ and HF, leading to $\text{Al}(\text{OH})_2\text{F}$, $\text{Al}(\text{OH})\text{F}_2$ and other intermediates as $\text{AlF}_{1.65}(\text{OH})_{1.35} \cdot n\text{H}_2\text{O}$, or in a general formula $\text{AlF}_{3-x}(\text{OH})_x$ [19].

The presence of $(\text{NH}_4)_3\text{AlF}_6$ and $\text{AlF}_{3-x}(\text{OH})_x$ in high fluorine content of FMA-20 catalyst suggest that AlF_3 could be formed according to both mechanisms in agreement with Rodriguez et al. [10]. However, the concentration of the NH_4F solution used for impregnation controls the $\text{Al}_2\text{O}_3/\text{NH}_4\text{F}$ ratio, which influences the proportion of these intermediate phases at last. And the above intermediate phases are amorphous and well dispersed at the surface of alumina support [16]. Rodriguez et al. also found that XPS analysis could get results with low fluorine content (>2 wt%) while XRD technique did not allow to get any information when fluorine content was lower than 13 wt%. The same results also

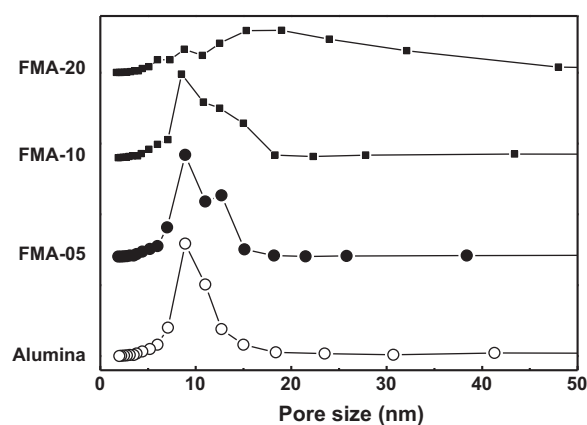


Fig. 2. Variation, with respect to fluorine content, of BJH pore distribution curves of fluorinated alumina modified with magnesium.

found in our work. For the fluorination method used in this manuscript is almost the same with Rodriguez, and the fluorine content is low (10 wt%), all these results suggest that effective modification of alumina with fluorine while AlF_3 also could not be detected by XRD analysis [16,20].

Since the catalytic performance of the individual catalysts also depends on the porous structure of the solid [1], the differences in the surface area and pore size distributions of the catalyst with different fluorine contents has been compared, the physical properties and pore geometry of these materials are given in Table 1 and Fig. 2, respectively. From Table 1, the solids lose surface area when the fluorine content increases. Fig. 2 shows that most of the pores are in the 8–30 nm size range and the distribution is relatively narrow. When the fluorine contents increase, the pore size distribution broadened compared with the alumina. The N_2 adsorption–desorption isotherms of the alumina without fluorine and FMA-20 (14.5 wt%) are presented in Fig. 3. The desorption step is slightly displaced to a higher p/p_0 value for the support with more fluorine content. Both the modification in the pores size distribution and the change of desorption p/p_0 value indicate an increase of the pores diameters induced by the fluorination. Above textural properties of the catalyst indicates that pores are penetrate into the body of the catalyst particles and the pore volume resides at the internal of the catalyst, the similar even larger porous structure is favourable to the condensation of aniline compared with the H-beta zeolite [21]. From Table 1, the difference between the fluorine content expected and the actual fluorine content indicates that some fluorine is lost during the preparation, which could be explained by an increasingly difficulty for reaction of fluorine with the surface aluminum atoms [12,22,23]. From powder XRD patterns of Fig. 1, even ammonium fluoride is maintained on the catalyst during the drying and sublimated

Table 1
Chemical analysis and textural properties of different fluorine content fluorinated alumina modified with magnesium.

Catalyst	Elemental content (wt%)		Surface area (m^2/g)	Pore vol. (mL/g)	Average pore size (nm)
	Fluorine	Magnesium			
None ^a	0	0	379	1.04	10.6
FMA-02	1.92	0.76	373	0.98	10.8
FMA-05	4.35	0.73	359	0.95	10.9
FMA-08	6.76	0.76	306	0.92	11.3
FMA-10	7.93	0.77	285	0.91	11.8
FMA-12	10.2	0.71	289	0.89	12.3
FMA-15	13.7	0.77	295	0.96	12.2
FMA-20	15.1	0.74	278	0.93	12.9

^a Pure alumina carrier without any modification.

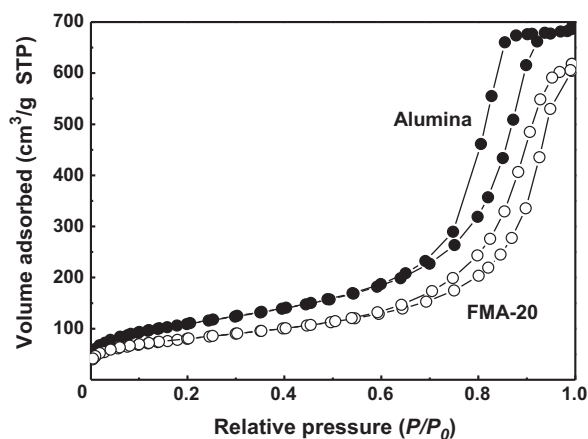


Fig. 3. N₂ adsorption-desorption isotherm at -195°C for the alumina and fluorinated (20 wt%) alumina modified with magnesium (0.75 wt%) catalysts.

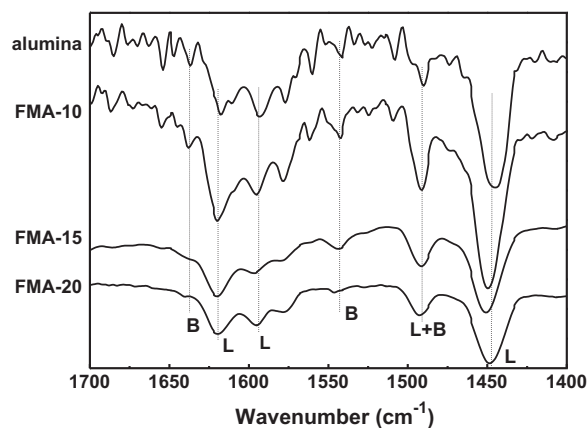


Fig. 4. Pyridine adsorption spectra of different fluorine content (ammonium fluoride) fluorinated alumina modified with magnesium L: band corresponding to Lewis sites, B: band corresponding to Bronsted acid sites, L + B: band corresponding to Lewis and Bronsted acid sites.

during calcination. The catalytic performance of the individual catalysts also relates to the number of these fluorinated active sites and the corresponding acid strength, to distinguish the Bronsted and Lewis acid sites, typical infrared spectra of pyridine adsorbed on the fluorinated alumina modified with magnesium catalysts are shown in Fig. 4.

For the pyridine adsorption FT-IR spectra of pure alumina shown in Fig. 4, peaks at $1447, 1594\text{ cm}^{-1}$ are representative of Lewis acidity [16]. For the spectra of fluorinated alumina, peaks at 1543 and 1637 cm^{-1} due to pyridinium ions reveal the presence of Bronsted acidity [14]. Evidence of this acidity is also shown by the band at about 1490 cm^{-1} , which is attributed to Lewis and Bronsted sites [24]. Increasing the fluorine content leads to an increase in Bronsted and Lewis acidity, as evidenced by the increase in the peak at 1543 cm^{-1} and 1447 cm^{-1} . Fig. 4 shows that the number of Bronsted and Lewis acid sites is reduced after rising with increasing of fluorine content. This occurs because portions of the surface hydroxyl groups of alumina are replaced by fluoride ions, which increases the electronegativity of the surface and consequently the acidity of the remaining hydroxyl groups [16,25].

2.2. Catalytic studies

Catalytic performance and related acid properties obtained for the catalysts modified with different alkaline, alkaline earth metals and H-beta zeolite at 350°C are given in Table 2.

As is shown in Table 2, pure alumina shows low concentration of Bronsted acid sites and Lewis acid sites, since incomplete

transformation of pseudoboehmite occurred during the calcination process, which contains water in the structure [26]. From Table 2, the catalyst activity and selectivity of pure alumina are poor. After the fluorination process, the catalytic performances increased dramatically, the concentration of Bronsted acid sites and Lewis acid sites of this catalyst is the highest among all the catalysts. The production of DPA depends not only on the structure of the heterogeneous catalysts but also on proper number of acid sites with medium acid strength [1]. During the fluorination of alumina, new Bronsted and Lewis acid sites will produce with new generated intermediates phases, such as $(\text{NH}_4)_3\text{AlF}_6$, $\text{AlF}_3-x(\text{OH})_x$, and $\text{AlF}_3 \cdot n\text{H}_2\text{O}$. The mobility of the protons of close OH groups is probably increased for hydroxide ions were substituted by fluoride ions. Very mobile hydrogen could be also generated for the formation of $\text{AlF}_3-x(\text{OH})_x$ due to the strong inductive effect of the gem-fluoride ions. In addition, adjacent hydrated $\text{AlF}_3 \cdot n\text{H}_2\text{O}$ results in even stronger acid sites [10]. By addition of fluorine content, Moreno et al. evidenced that the total number of Bronsted acid sites increases, especially the medium and strong Bronsted acid sites [14]. These increased Bronsted acid sites, especially medium ones, are very suitable for the production of DPA [1]. Therefore, fluorination of alumina could improve the catalytic activity for this reaction. These results suggests that fluorinated compounds such as $(\text{NH}_4)_3\text{AlF}_6$, $\text{AlF}_3-x(\text{OH})_x$, and $\text{AlF}_3 \cdot n\text{H}_2\text{O}$ are important catalytic active intermediates [16]. With the modification of different alkaline and alkaline earth metals, both conversion and selectivity results of fluorinated alumina strongly depends on the type of the metals while the catalyst modified with magnesium showed the

Table 2

Catalytic performance and related acid properties of fluorinated alumina modified with different alkaline, alkaline earth metals and H-beta zeolite.^a

Element	Metal content (wt%) ^b	Metal content (mmol/g)	Lewis sites (mmol/g)	Bronsted sites (mmol/g)	Aniline conversion (%)	DPA selectivity (%)
Li	0.22	0.31	0.35	0.23	28.6	96.7
Na	0.72	0.31	0.31	0.19	19.0	95.5
K	1.20	0.31	0.28	0.11	12.8	94.5
Mg	0.75	0.31	0.42	0.26	30.5	95.7
Ca	1.25	0.31	0.37	0.21	24.0	91.6
Ba	4.30	0.31	0.35	0.17	20.6	87.9
F ^c	–	–	0.43	0.29	28.4	88.5
None ^d	–	–	0.26	0.13	22.4	68.5
H-beta ^e	–	–	0.37	0.33	28.2	95.1

^a The reaction proceeded at 350°C for 4 h, LHSV = 0.2 h^{-1} with H₂ at atmosphere pressure, fluorine content 10 wt%.

^b Theoretical contents of alkaline and alkaline earth metals macerated on the fluorinated alumina.

^c Alumina modified with fluorine (10 wt%).

^d Pure alumina calcined from pseudoboehmite in a stream of air at 550°C for 4 h.

^e H-beta (Si/Al = 12.5), calcined in a stream of ammonia (5%) in nitrogen at 350°C followed by ion-exchange with NaNO₃ and further calcination in a stream of air at 500°C .

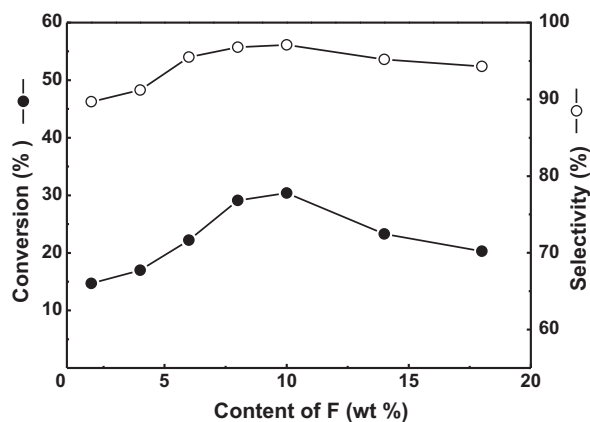


Fig. 5. Catalytic performance of different fluorine content (ammonium fluoride) fluorinated alumina modified with magnesium.

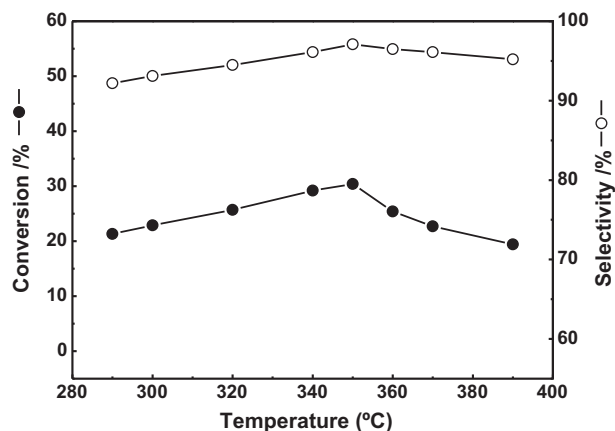


Fig. 6. Effect of temperature on catalytic performance of the fluorinated (10 wt%) alumina modified with magnesium (0.75 wt%) catalyst. Reaction condition: reaction temperature = 350 °C, LHSV = 0.2 h⁻¹ with H₂ at atmosphere pressure.

best catalytic performances, even higher than H-beta zeolite. On the other hand, fluorinated alumina modified with sodium, potassium, or barium showed significantly lower activity. These differences in the catalytic activity can be probably related to the substantial different structures of the individual catalysts and to their acidic properties [1,27]. The alumina with high surface area and large pore diameter was used in the catalyst, and it seems that this specific pore structure is appropriate for the synthesis of diphenylamine. Larger

cavities in intersections of the fluorinated alumina would allow for the formation of bulky intermediates, products or coke precursors, which increased the catalytic activity. The high catalytic activity and selectivity is also related to a proper number and strength of acid sites [27,28]. The presence of strong acid sites is responsible for the formation of by-products and thus for a lower selectivity of aniline condensation [1]. Since the mol ratio of alkaline and alkaline earth metal added in the fluorinated alumina was the same (0.31 mmol/g), only the alkalinity of metals varies from magnesium, lithium to calcium, sodium, barium and potassium, so these metals could preferentially cover and neutralize nearly the same amount Bronsted acid sites (0.29 mmol/g) with different alkalinity. Therefore, these alkaline and alkaline earth metals affected the strong Bronsted acid sites greatly, making strong Bronsted acid sites change to medium even weak Bronsted acid sites, and the overall concentration of Bronsted acid sites decreased (Table 2). This also has been confirmed by Moreno et al. [14]. Through IR characterization by adsorption of d₃-acetonitrile, we also found that the catalytic activity decreased with the enhanced alkalinity of metals, but the decline of the catalytic selectivity is not obvious, which indicates that the condensation of aniline was rather close to the thermodynamic equilibrium value. The decrease in the concentration of acid sites in catalysts influences only their activity, and the selectivity to diphenylamine was influenced by the strength of the acid sites. Strong acid sites favour not only the desired aniline condensation but also the formation of side products [1]. Modification with strong base cations, such as calcium, sodium, barium or potassium, reduced the strong Bronsted acid sites intensively, which reduced the formation of side products, thereby the catalytic selectivity of DPA increased. The modification with these strong base cations reduced not only the strength of the acid sites, but also the concentration of Bronsted acid sites, compared with weak base cations, such as magnesium and lithium, the concentration of acid sites also evidenced the same results by the method from Witcherlova et al. in Table 2 [29]. There is another article also raised the similar conclusion [1]. With the combined adjusting of fluorine and different alkaline and alkaline earth metals, the type of acid sites was greatly influenced, and the catalytic selectivity for condensation of aniline to DPA was little changed. And the concentration of acid sites affects the catalytic activity intensively.

In order to see the influence of the fluorine content to the FMA catalysts on catalyst performance, the alumina is loaded with different fluorine contents, and then change concentration of the maceration extract, the suspended liquid is mixed slowly under the room temperature, appraise the performance of the catalysts under equal conditions. The results are shown in Fig. 5. From Fig. 5,

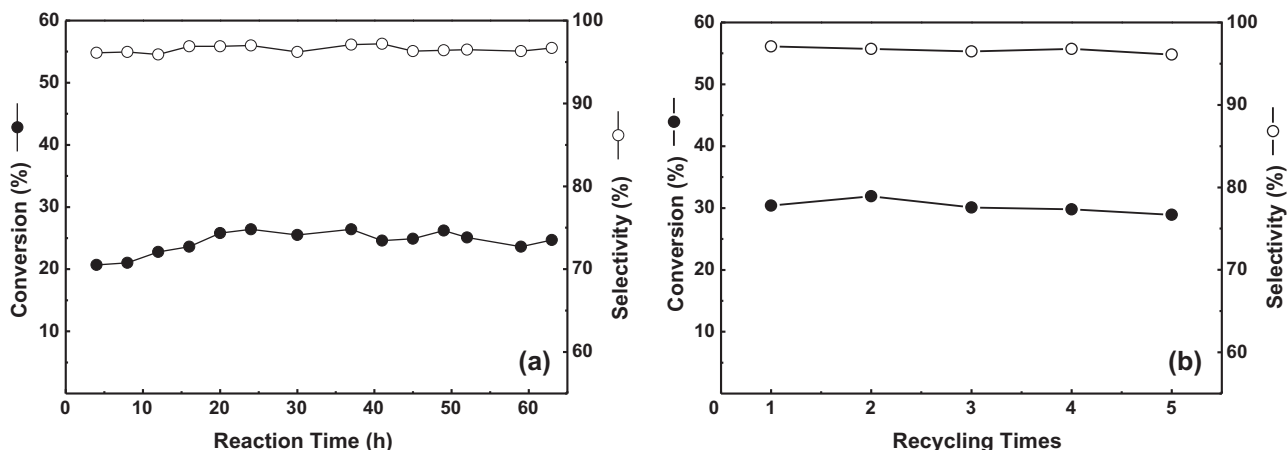


Fig. 7. Catalytic performance of the fluorinated (10 wt%) alumina modified with magnesium (0.75 wt%) with a changes of catalytic activity, and b recycling test. Reaction condition: reaction temperature = 350 °C, LHSV = 0.2 h⁻¹ with H₂ at atmosphere pressure.

the catalysts modified with different fluorine contents have different conversion rate and selectivity of DPA. With increasing of fluorine content, the activity of FMA catalyst is reduced after rising. The catalyst has the best activity when fluorine content is in 10 wt%. The high activity of the catalyst may relate to the fact that the catalyst has better acid distribution [1]. The modification of ammonium fluoride and magnesium changes the acid distribution of alumina, makes the catalyst have the suitable acid intensity for production of DPA. The modification also reduces the formation of the accessory substances, avoids the deposit of coke, and improves the performance of the FMA catalyst at last [30]. Since the thermodynamic equilibrium of condensation of aniline to DPA could be affected by reaction temperature, the catalytic behaviour for the aniline condensation as a function of the temperature was researched, and the results were given in Fig. 6. From Fig. 6, the conversion is controlled by the thermodynamic equilibrium when the reaction temperature is higher than 350 °C. Finally, it could be concluded that under such conditions the reaction is not thermodynamically limited and that higher conversions could be obtained by increasing the contact time [31]. Attempt could therefore be made to correlate the catalytic activity patterns to some physico-chemical characterization.

For the most active catalyst, FMA-10, the stability and reusability of their catalytic performance in condensation of aniline to DPA was tested, the results are given in Fig. 7.

From the entire test showed in Fig. 7a, the activity of catalyst obtained by impregnation of support was increasing for the first 30 h, and then the catalyst showed stable work. Through the reaction of more than 60 h, the conversion of aniline and selectivity of DPA do not have great change, which indicates that the stability of the catalyst is good [13]. Moreover the catalyst is reusable for at least five catalytic runs only under the calcination at 500 °C for 4 h before the recycling test (Fig. 7b). Fig. 7b shows activities and selectivities obtained after calcination and by charging a new continuous flow reaction system. The slight decrease observed in activity could therefore be due to a feeble poisoning of the catalyst surface and the lost of fluorine content [22].

3. Conclusions

In this report we successfully elaborated the preparation of fluorinated alumina simply and eco-friendly modified with different alkaline and alkaline earth metals. With the modification of magnesium, fluorinated alumina showed the higher catalytic activity and selectivity for condensation of aniline to diphenylamine than other alkaline, alkaline earth metals and the H-beta zeolite. The function of magnesium was studied in detail. It could decrease the strong acid sites of fluorinated alumina without influencing the concentration of total acid sites. The high catalytic performance of fluorinated alumina with magnesium is greatly related to the pore geometry with high surface area, large pore size and high concentration of acid sites with an intermediate acid strength. A proper number of acid sites with an intermediate acid strength could be controlled easily using the combination adjusting of the fluorine and magnesium. The catalyst could at least maintain its catalytic performance for 65 h and reuse for 5 times at the reaction temperature of 350 °C.

4. Experimental

4.1. Synthesis of fluorinated alumina modified with different alkaline and alkaline earth metals

Pseudoboehmite (α -AlOOH, BET surface area 379 m²/g, average pore diameter 10.6 nm) is used as the precursor of γ -Al₂O₃ (short for alumina) after calcination at 550 °C in the presence of air for 4 h, which was provided by the catalyst factory of Nankai University.

All the chemicals were procured from Tianjin Chemical Corp., China (analytical grade) and used without further purification. For the typical catalyst preparation process, a certain weight of alkaline or alkaline earth metal nitrate and alumina were blended using 60 mL distilled water in 400 mL glass beakers with 4 h for agitation. Then they were put into ovens with the temperature of 80 °C to dry the water, followed by calcinations at 550 °C in the presence of air for 4 h. The repetitious modifications for one catalyst were the same as above. The percentages indicate the weight of elements (fluorine and metals) to the weight of alumina. For example, F(10%)-Mg(0.75%)/alumina (short for FMA-10) denotes that 4 g alumina was first impregnated by 0.78 g of ammonium fluoride which contains 0.4 g fluorine. After drying at 90 °C for 12 h and calcination at 550 °C for 4 h, it was then impregnated by 0.33 g of magnesium nitrate which contains 0.031 g magnesium. The repetitious drying and calcination process for the catalyst were the same as above. The catalyst was pressed with the pressure of 15 t when all the modifications were finished. Then using sieves granular catalysts with 20–40 mesh can be obtained for experiments.

4.2. Characterization methods

X-ray powder diffraction (XRD) patterns of the dry samples were performed on D/max 2500 diffractometer with Cu K α radiation (λ = 0.154 nm). Typically, the data were collected from 10° to 80° with a resolution of 0.2°. N₂ adsorption–desorption isotherms were obtained at –196 °C on a Micromeritics Tristar 3000 sorptometer. Samples were outgassed at 150 °C for a minimum 12 h prior to analysis. The experimental data were further processed by the BET equation for surface areas and by the BJH model for pore size distributions. The acidities of pure alumina, fluorinated alumina modified with magnesium and commercial H-Beta zeolite catalysts were measured by means of FT-IR analysis of chemisorbed pyridine on a Magna Model 560 spectrophotometer (Nicolet, U.S.A.). The samples were calcined at 500 °C and then exposed to liquid pyridine at 80 °C for 4 h and then kept at room temperature overnight so as to allow the base to permeate the samples. The concentrations of Bronsted and Lewis sites were estimated by the adsorption of d₃-acetonitrile followed by the same FT-IR methods. The samples were activated at 500 °C overnight under vacuum, then exposed to d₃-acetonitrile with a partial pressure of about 1000 Pa. The adsorption was for 1 h followed by desorption to vacuum for another 0.5 h. The fluorine and magnesium contents have been determined for catalysts calcined at 550 °C on a Thermo Jarrell-Ash ICP-9000 inductive coupled plasma emission spectrometer.

4.3. Catalytic activity measurements for condensation of aniline to diphenylamine

The reactor system was a fixed-bed, vertical, flow-type reactor made of stainless steel tube of 40 cm in length and 8 mm in diameter. The stainless steel reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. The quantity of modified alumina used in each run was 1 g with the mesh of 20–40. The catalyst was placed in the middle of the reactor and supported by a thin layer of glass wool under it. The raw stuff of aniline was fed into the reactor by a syringe pump that could be operated at different flow rates under atmospheric pressure. The experimental conditions including different granular size and space velocity was performed, and the best reaction conditions could be considered as belonging to the chemical kinetic regime with proper granular size of the catalysts and space velocity of the condensation reaction. The effects of the reaction temperature and time were investigated.

The products were condensed in a water-cooled condenser at hourly intervals and analyzed in a SP-502 gas chromatograph (Shanghai Hongtu Instruments Co. Ltd., China) equipped with 0.25 mm \times 50 m capillary column.

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