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A convenient preparation method for synthesizing formamidine utilizing sulfated zirconia

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Sulfated zirconia is able to effectively catalyze the reaction between aniline and trimethyl orthoformate to produce formamidine with a product yield of 97% at 313 K. *N*-phenylformimidate is proposed as the reaction intermediate, which reacts further with aniline to produce formamidine. Less degree of acid sites poisoning by the reaction mixture due to the weaker acidity of sulfated zirconia as well as its mesoporosity seem to play important role in this catalyzed reaction.

KEY WORDS: sulfated zirconia; formamidine; trimethyl orthoformate.

1. Introduction

It was known that several metal oxides such as ZrO_2, TiO_2, Fe_2O_3, SnO_2, Al_2O_3, HfO_2, and SiO_2 after being impregnated with sulfuric acid solution and calcined at elevated temperatures became solid acids with a fairly strong acid strength [1]. These solid acids contained mostly Lewis acid sites and possessed a mesoporous structure after high temperature calcination. As the composition of the gasoline was reformulated worldwide, these sulfated metal oxides (SMO) have been receiving intensive research interest because of their high efficiencies in catalyzing paraffin hydroisomerization and alklation reactions [1–3]. On the other hand, unlike other well-developed solid acids such as zeolites, Nafion-H and heteropoly acids, current applications of SMO solid acids were limited primarily to petroleum chemistry [2,3], and very few have been reported for other research areas such as the synthetic organic chemistry. In this paper, we would like to report a highly active and selective one-step catalytic reaction for synthesizing formamidine from trimethyl orthoformate (TMOF) and aniline over sulfated zirconia (equation 1).

$$2ArNH_2 + HC(OCH_3)_3 \rightarrow ArN{=}CHNHAr + 3CH_3OH \tag{1}$$

Formamidine, ArN=CHNHAr, and their anion derivatives are common ligands frequently used in coordination chemistry, in which they were found binding to transition metals with monodentate, chelating or bridging bonding modes [4–9]. Roberts had utilized several organic and mineral acids to catalyze the formation of formamidine and found that the major reaction product would depend on the reaction condition and the catalyst used to catalyze the reaction [10–13]. The primary reaction product of methyl orthoformate and a primary amine in the presence of an acid catalyst below 413 K was methyl *N*-phenylformimidate, $ArN{=}CHOCH_3$ (equation 2.1). In the presence of excess of amine, formamidine was produced by further reaction of methyl *N*-phenylformimidate with another molecule of aniline (equation 2-2). At a temperature higher than 413 K, *N*-methylformanilide ($ArNCH_3CH{=}O$) was produced through the isomerization of methyl *N*-phenylformimidate (equation 2.3). The reaction path is summarized below in equation 2.

$$ArNH_2 + (CH_3O)_3CH \rightarrow ArN{=}CHOCH_3 + 2CH_3OH \tag{2.1}$$

$$ArN = CHOCH_3 + ArNH_2 \rightarrow ArN = CH - NHAr + CH_3OH \tag{2.2}$$

$$ArN = CHOCH_3 \rightarrow ArNCH_3CH = O \tag{2.3}$$

Interestingly, we had found that under an aniline-deficient condition the most reactive SO_4^{2-}/ZrO_2 produced an almost quantitative yield (97%) of formamidine as the major reaction product after an overnight reaction at 313 K. Methyl *N*-phenylformimidate yield was less than 3% and no *N*-methylformanilide was found in the product mixture. Furthermore, sulfated zirconia displayed a significantly higher activity than a few molecular sieve catalysts (HM and β- zeolites) we had tested. We attributed such high activity to the combination effect of persisting acidity (after self-poisoning of acid sites by the reaction mixture, see below) and mesoporosity of sulfated zirconia.

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2. Experimental

Sulfated metal oxides were prepared according to the method reported previously, and except for SO_4^{-2}/Al_2O_3, all SMO were prepared by immersing the appropriate metal hydroxides into a sulfuric acid solution [14]. The mixture was filtered, dried, and calcined at a proper temperature to produce SMO. The metal hydroxides were obtained by precipitating their metal salt solutions with aqueous ammonia (29.5%). The metal salts used to prepare these SMO were $ZrOCl_2{\cdot}8H_2O$, $Ti[OCH(CH_3)_2]_4$, $SnCl_4{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, and $H_fCl_4{\cdot}$ SO_4^{-2}/Al_2O_3 was prepared by immersing γ- Al_2O_3 in 1.60 M sulfuric acid solution, followed by calcining at 823 K.

Threeβ-zeolites (CP811E-75, CP811E-150, CP811C-300) with different SiO_2 to Al_2O_3 ratio were obtained from PQ corporation and also tested for the catalytic activity. These beta zeolites are all in hydrogen form and were calcined at 573 K for 3 h before use. Three mordenite catalysts (also from PQ) with different SiO_2 to Al_2O_3 ratio and cations were also examined in this paper. The hydrogen form mordenite (CBV90A) was calcined at 573 K for three hours before use. The ammonium form mordenite (CBV21A) was decomposed at 723 K for 3 h in order to transform into hydrogen form. The sodium form mordenite (CBV10A) was ion exchanged in HCl solution to obtain the hydrogen form. The ion-exchange procedure was the following: 10.0 g of the mordenite were dispersed in 100 mL of 1.0 M HCl solution and refluxed for 1.0 h. Such procedure was repeated for three times. The product mixture was filtered and washed in the deionized water. The washing should continue until the filtrate containing no chloride ions when tested with $AgNO_3$ solution. The exchanged mordenite was dried at 373 K and calcined at 573 K for three hours before use.

A typical reaction procedure was the following: 45.1 mmol of aniline were mixed with excess trimethyl orthoformate (130.2 mmol). This mixture was added to a 0.30 g of SMO catalyst in a round-bottom flask and reacted with stirring at 313 K for a specific amount of time. The product mixture was than separated from the SMO solid acid catalyst by filtration. The filtrate was analyzed by HP6890 GC utilizing internal standard method. GC/Mass equipped with a HP-5973 mass selective detector (MSD) was used to identify the reaction product, and IR and NMR were also used for identification wherever was necessary

Temperature programmed desorption (TPD) experiments using ammonia as adsorbate and a qudra-pole mass spectrometer as detector were performed on these solid acid catalysts to compare their acidities. Before introducing NH_3, 50 mg of catalyst was dried at 573 K for 3.0 h in air flowing at a rate of 30 mL min^{-1}. The adsorption step was conducted at 373 K using a flowing NH_3 of 30 mL min^{-1} for 30 min. After adsorption, the gas flow was switched to 30 mL min^{-1} of He for 30 min to flush out the excess NH_3. The reactor temperature then was raised to 1073 K at a rate of 10 K min^{-1} in a flowing He of 30 mL min^{-1}. All SMO catalysts were calcined at 723 K for 3 h before the reaction. XRD spectra of sulfated zirconia calcined at different temperatures were recorded with Shimadzu Lab-X XRD-6000 spectrometer (Fe K_α, $\lambda = 1.93604$ Å). BET surface area and pore diameter were obtained with Micromeritics ASAP 2010 surface area and porosimetry analyzer.

3. Results and discussion

Table 1 shows the activities and formamidine selectivities of various SMO catalysts and H-form zeolites at the first hour of reaction. As can be clearly seen from the table, SO_4^{-2}/ZrO_2 is the most productive catalyst among all the solid acids tested with an aniline conversion of 35% and a formamidine selectivity of 98%. Other solid acids such as H-mordenite (CBV-21A), β-zeolite (CP811E-75), $SO_4^{-2}/$ Al_2O_3 and SO_4^{-2}/TiO_2 are roughly half as active as SO_4^{-2}/ZrO_2, with conversions between 15% to 20% and formamidine selectivities better than 97%. Figure 1 depicts the variation in aniline conversion and formamidine selectivity with time over SO_4^{-2}/ZrO_2 catalyst. Interestingly, over SO_4^{-2}/ZrO_2 catalyst the formamidine yield increased linearly with the reaction time initially and a constant high formamidine selectivity of >98% was obtained during the entire reaction period. At a temperature of 313 K and ambient pressure, SO_4^{-2}/ZrO_2 produced a formamidine yield of 97% after an overnight reaction. In addition to a small amount of methyl *N*-phenylformimidate (*m*/*e* = 135) as the other product, MSD indicated the presence of trace of methyl formate (*m*/*e* = 60) and *N*-formanilide (ArNHCH = O, *m*/*e* = 121) as other by-products. These by-products offer valuable clues to the reaction path of this acid-catalyzed reaction (see below).

Due to the special structural characteristics of zeolites as solid acid catalysts, they display interesting catalytic properties during reactions with hydrocarbon molecules (15). It is true that zeolites can be used as true molecular sieve catalysts but they are still limited in pore size and are only suitable to catalyze the reaction involving molecules smaller than 15 Å. Therefore, even the large pore zeolite such as β-zeolite does not favor the formation of large molecules such as formamidine and displays a poorer activity than SO_4^{-2}/ZrO_2 in this catalyzed reaction as shown in table 1. Zeolites with a high Si/Al ratio such as the three β-zeolites and HM (CBA90A) have highly hydrophobic surfaces, which are not beneficial for this catalyzed reaction (16). The Si/Al ratio has been shown to be a critical factor in determining the acid strength of the zeolite. However, there is no clear trend in Si/Al ratio toward the catalytic activity in table 1. It turns out that acid strength is not a crucial

Table 1
Comparison of activities and selectivities of different catalysts[a]

Catalyst	SiO_2/Al_2O_3	Conv.(%)	Selec.(%)	Turnover frequency
SO_4^{-2}/ZrO_2		35	98	0.58
SO_4^{-2}/TiO_2		15	97	
SO_4^{-2}/Al_2O_3		17	98	
SO_4^{-2}/Fe_2O_3		7	79	
SO_4^{-2}/HfO_2		9	83	0.24
SO_4^{-2}/SnO_2		10	80	
HM(CBV21A)	20	20	99	0.045
HM(CBV90A)	90	12	94	
HM(CBV10A)	13	7	93	
β- zeolite (CP811E-75)	75	17	98	
β- zeolite (CP811E-150)	150	12	93	
β- zeolite (CP811C-300)	300	13	94	

[a] Experimental condition: 45.1 mmol aniline and 130.2 mmol trimethyl orthoformate mixed with 0.3 g of catalyst at 313 K for 1.0 h.

factor to influence the catalytic activities of this reaction (see below for more detail discussion).

Preliminary structural analyses on the sulfated zirconia catalyst were performed using low temperature N_2 adsorption and XRD. Variation in phase composition and physical properties of SO_4^{-2}/ZrO_2 calcined between 673 and 973 K and pure $Zr(OH)_4$ calcined at 873 K are summarized in figure 2 and table 2, respectively. As observed by many other researchers [1–3], in addition to enhance the acidity of zirconia, sulfate group also retards the crystallization of zirconia and transformation of tetragonal phase to monoclinic phase as the calcination temperature is increased. Therefore, the active SO_4^{-2}/ZrO_2 catalyst (calcined at 873 K) has a tetragonal phase and a significantly higher surface area (115 $m^2\ g^{-1}$) than the non-sulfated ZrO_2, which has a monoclinc phase and a surface area of 25 m^2g^{-1}.

We had also examined the strength and number of the acid sites in three selected solid acids (SO_4^{-2}/ZrO_2, HM(CBV21A) and SO_4^{-2}/HfO_2) using TPD/Mass with NH_3 as the acidity probe in order to investigate the nature of this catalytic reaction. TPD/NH_3 had revealed interesting acidic properties of these solid acids. Using $m/e = 16$ signal to monitor the presence of NH_3, TPD indicates that HM catalyst has two well resolved desorption peaks at 450 and 783 K in figure 3, respectively. On the other hand, SO_4^{-2}/ZrO_2 and SO_4^{-2}/HfO_2 catalysts display a wide range of acidities, with NH_3 desorption peak temperatures ranging from 413 to 973 K.The peak at 450 K (temperature range between 373 and 547 K) in HM is widely regarded as weakly adsorbed NH_3 and plays no role in the acid-catalyzed reaction. Only those acid sites associated with the second desorption peak at 783 K (temperature range between 547 and 1073 K) have enough acid strength to participate in the acid-catalyzed reaction, and these acid sites amount to 186 μmol/g in HM (out of a total of 286 μmol/g). Following such guideline for dividing the acid strength, the acid sites with desorption temperature > 547 K in SO_4^{-2}/ZrO_2 and SO_4^{-2}/HfO_2 catalysts are 25.4 μmol/g (out of a total of 41.8 μmol/g) and 15.6 μmol/g (out of a total of 25.6 μmol/g), respectively. Judging from the number and the strength distribution of these acid sites in figure 3, it is surprised to note that the less acidic SO_4^{-2}/ZrO_2 is more active than the most

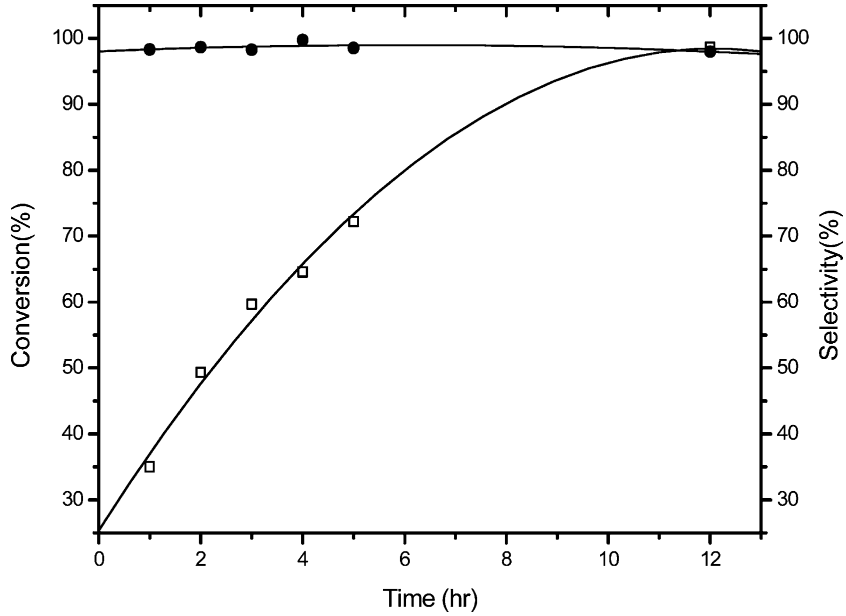


Figure 1. The variation of aniline conversion (☐) and formamidine selectivity (●) with time over 0.3 g of SO_4^{-2}/ZrO_2 catalyst at 313 K using 45.1 mmol of aniline and 130.2 mmol of TMOF.

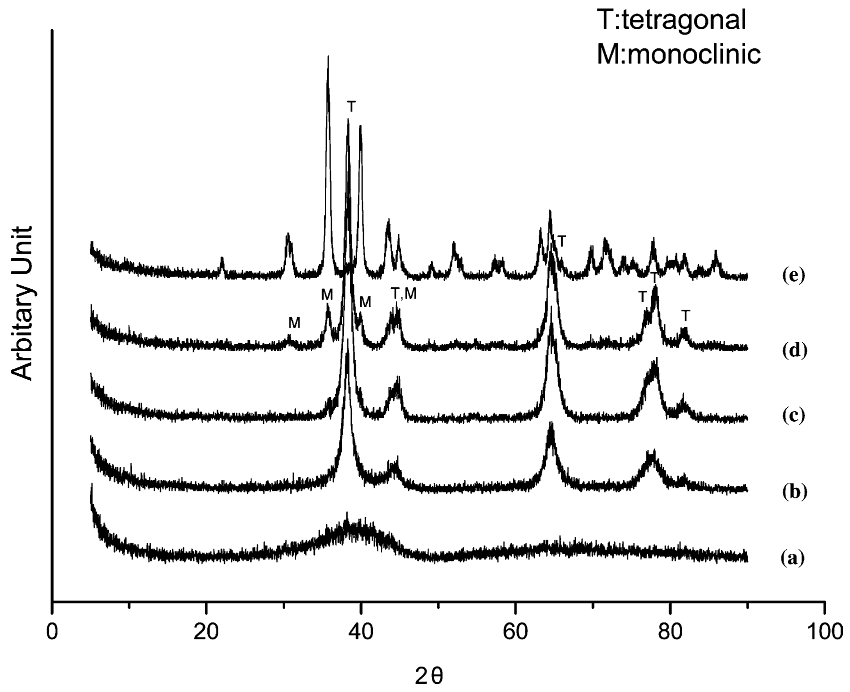


Figure 2. XRD spectra of sulfated zirconium hydroxide calcined at different temperatures (A) 673 K, (B) 773 K, (C) 873 K, (D) 973 K, (E) $Zr(OH)_4$ calcined at 873 K.

acidic HM catalyst. Utilizing the acid site number (for those with desorption temperature >547 K) acquired by TPD, the turnover frequencies were calculated for SO_4^{-2}/ZrO_2, HM (CBV21A) and SO_4^{-2}/HfO_2 (table 1). The result indicates that the turnover frequency of SO_4^{-2}/ZrO_2 is an order magnitude higher than HM (CBV21A). This rationalization of such contradiction is provided in the following.

The participation of the acid sites is obviously required in this reaction since SO_4^{-2}/ZrO_2 catalyst with a higher concentration of the acid site is more active than SO_4^{-2}/HfO_2 with a lower concentration of acid sites, considering that the distribution of the strength of acid sites is about the same in two catalysts as depicted in Figure 3. However, there must be some other factors involved in the reaction to account for the inferior catalytic performance of HM. We suggest that the poisoning of the strong acid sites (with desorption temperature >547 K) and the pore size constraint of HM should be taken into account to explain the poorer catalytic activity of HM. With nitrogen atom(s) having a pair of lone electrons (a Lewis base) in the molecular structure, it is likely that aniline and/or formamidine will poison the strong acid sites in these solid acids and reduce their catalytic activities. Nonetheless, some acid sites with medium acidity (with desorption temperature >547 K) must survive the poisoning as evidenced by the fact that there is a considerable difference in conversion between SO_4^{-2}/ZrO_2 and SO_4^{-2}/HfO_2 (35% versus 9%). Such poisoning effect by the reactant and/or product was supported by reaction results utilizing substituted aniline.

Table 2
Physical properties of SO_4^{-2}/ZrO_2 calcined at different temperatures

Catalyst/ Temp.(K)[a]	Phase[b]	BET S.A.(m^2g^{-1})	Pore diameter[c](Å)
SZ/673	A	246	28
SZ/773	T	268	33
SZ/873	T	115	48
Z/873	M	25	211
SZ/973	M,T	64	62

[a] SZ:sulfated zirconium hydroxide , Z: zirconium hydroxide.
[b] A:amorphous, T:tetragonal M:monoclinic.
[c] Adsorption average porediameter(4V/A by BET).

Under the same reaction condition, less basic 4-cyano aniline produced a product yield of 49% in 15 min. over SO_4^{-2}/ZrO_2 while the more basic 4-methoxy aniline only produced a product yield of 10% after an overnight reaction at 353 K. Our rationalization is that the less basic 4-cyano aniline must poison a smaller fraction of the acid sites (with desorption temperature >547 K) in SO_4^{-2}/ZrO_2 and resulted in a higher product yield in a shorter reaction time than aniline. On the other hand, more basic 4-methoxy aniline must poison a higher fraction of acid sites in SO_4^{-2}/ZrO_2 and could only obtain a lower product yield than aniline even at a higher reaction temperature of 353 K and a longer reaction time. The used catalyst did develop some color after reaction in the aniline/TMOF mixture, but the color change did not seem to severely impair the catalytic activity of SO_4^{-2}/ZrO_2. We had filtered and collected the catalyst after the reaction, and re-examined the catalytic activity of the used catalyst. Such catalyst

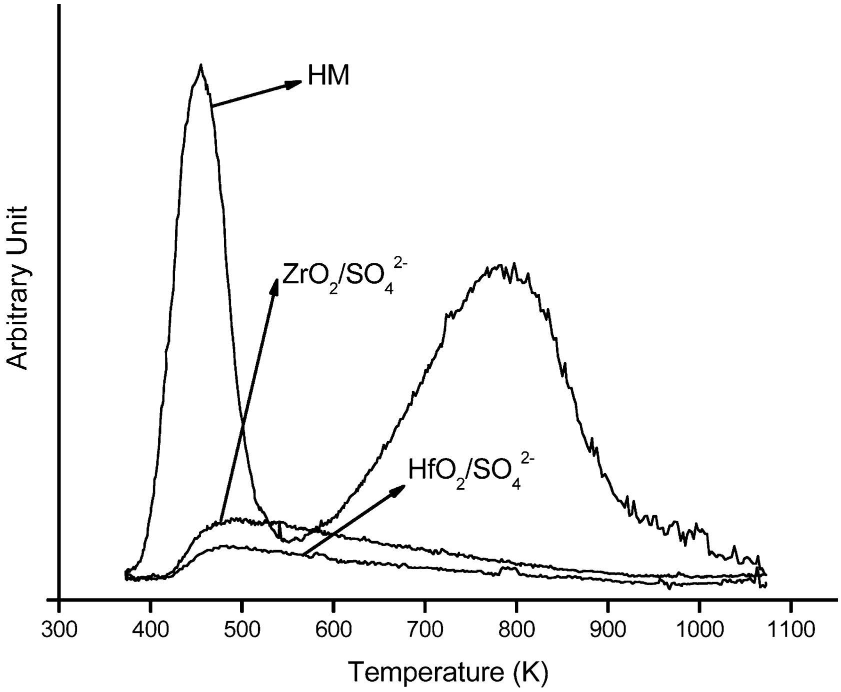


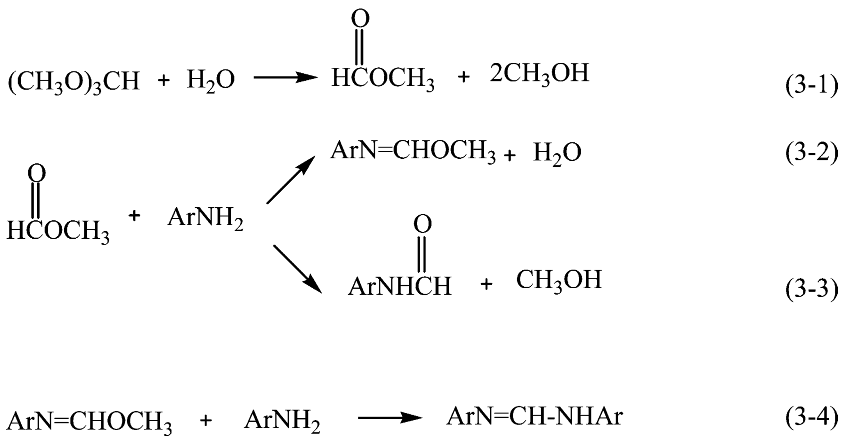
Figure 3. TPD/NH_3 spectra (m/e = 16) for SO_4^{2-}/ZrO_2, SO_4^{2-}/HfO_2 and HM (CBV21A) solid acids.

could produce a formamidine yield of 32% under the same reaction condition as in table 1. Calcining SO_4^{-2}/ZrO_2 at 773 K regained the original white color and catalytic activity of the SMO catalyst.

It is quite obvious that even after the poisoning of its acid sites, HM should still contain a higher concentration of acid site (with desorption temperature > 547 K) than SO_4^{-2}/ZrO_2 according to the TPD results in figure 3. Therefore, in addition to the poisoning effect described above, we should also consider the pore size constraint on the diffusion of large molecular size product such as formamidine in the HM framework. HM is a microporous solid acid with a 7.0 Å × 6.7 Å elliptical pore, while SO_4^{-2}/ZrO_2 is mesoporous with a BJH desorption pore diameter around 35 Å (for the catalyst calcined at 873 K). The much smaller pore size of HM will restrict the diffusion of formamidine out of the zeolite framework. During the preparation of dimethyl acetal from carbonyl compounds and TMOF, our laboratory had observed that while both catalysts could achieve a conversion of 100%, SO_4^{-2}/ZrO_2 took only 15 min. to complete the reaction but HM catalyst would require 120 min. [14]. We attributed this activity difference to the slow diffusion of bulk dimethyl acetal out of HM framework. Similarly, in the synthesis of dimethylacetal of different molecular sizes, Corma had reported that while β-zeolite was the most active catalyst, its activity strongly decreased when increasing size of the reactants, but the catalytic activity of the mesoporous MCM-41 (with 35 Å pore) remained practically unchanged [17]. They attributed this to the weaker adsorption and faster diffusion of the bulky products in MCM-41. Because of the existence of such pore size constraint, it is quite possible that some of formamidine were formed from acid sites located on the external surface of HM.

We propose that this acid-catalyzed reaction could proceed by the following reaction sequence over SO_4^{-2}/ZrO_2 catalyst in scheme 1. In the first step of the reaction (equation 3.1), TMOF was hydrolyzed to methyl formate and two equivalents of methanol. This reaction occurred quantitatively at 313 K for 1:1 TMOF/H_2O mixture as we had tested over sulfated zirconia. The methyl formate then reacted with aniline to form methyl N-phenylformimidate in the second step (equation 3.2). Alternatively, the reaction between methyl formate and aniline might lead to the formation of *N*-formanilide (equation 3.3). TMOF is a mild and effective dehydrating reagent to drive the formation of C = N bond (imine formation) in equation 3.2 [18]. Therefore, in the presence of TMOF, the reaction rate of equation 3.2 should be much faster than step 3.3 at 313 K. As a result only trace of *N*-formanilide could be formed. In the final step, methyl *N*-phenylformimidate combines with another molecule of aniline to produce formamidine equation 3.4. The rate of this reaction is fast in the presence of a trace of acid as reported in the literature [19,20].

Interestingly, under the aniline-deficient condition our reaction did not stop at step 3.2 to produce methyl *N*-phenylformimidate as the main reaction product like Roberts reported. This is probably due to the poisoning described above so that on SO_4^{-2}/ZrO_2 catalyst surface, there already exists a high concentration of aniline and the further reaction between methyl *N*-phenylformimidate and aniline can easily take place.



$$(CH_3O)_3CH + H_2O \longrightarrow \overset{O}{\overset{\|}{H C}}OCH_3 + 2CH_3OH \quad (3\text{-}1)$$

$$\overset{O}{\overset{\|}{H C}}OCH_3 + ArNH_2 \longrightarrow ArN{=}CHOCH_3 + H_2O \quad (3\text{-}2)$$

$$\overset{O}{\overset{\|}{H C}}OCH_3 + ArNH_2 \longrightarrow ArNH\overset{O}{\overset{\|}{C}}H + CH_3OH \quad (3\text{-}3)$$

$$ArN{=}CHOCH_3 + ArNH_2 \longrightarrow ArN{=}CH\text{-}NHAr \quad (3\text{-}4)$$

Scheme 1. The reaction sequence for the formation of formamidine.

4. Conclusions

Mesoporous sulfated zirconia could effectively and selectively catalyze the reaction between aniline and TMOF to produce formamidine under a mild reaction condition. The self-poisoning of the acid sites by reactant and/or products and the smaller pore size of zeolite catalyst makes SO_4^{-2}/ZrO_2 more active than HM and beta zeolites. Sulfated zirconia seems to be a more effective solid acid catalyst for acid-catalyzed reactions involving large molecules.

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