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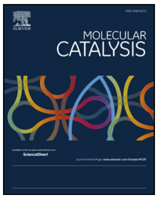

Ru/HZSM-5 as an efficient and recyclable catalyst for reductive amination of furfural to furfurylamine

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ABSTRACT

Furfurylamine converted from biomass-based platform molecules furfural was proven a significant intermediate in the synthesis of different valuable compounds. The combination of Ruthenium with HZSM-5 was acted as an excellent selective and reusable catalyst for the reduction amination of furfural with environmentally friendly ammonia and hydrogen. Incorporation of Ru species into HZSM-5 had a significant enhancement to the acid sites of Ru/HZSM-5. The Ru/HZSM-5(46) catalyst with optimized acid sites and interaction of the Ru-O-Al bond displayed an excellent catalytic performance, producing 76 % yield of furfurylamine at only 15 min, and could be recycled five times without loss of performance. Synergistic effect between RuO_2 and metallic Ru in the Ru/HZSM-5 catalyst facilitated the reduction amination of furfural.

1. Introduction

N-containing compounds, especially for primary amines, are important building blocks used widely for the preparation of surfactants, dyes, polymers, and agrochemicals [1–4]. Compared to other alternative feedstock, there are broader implications when it comes to the chemical synthesis of valuable N-containing compounds from biomass, which may be used as a promising strategy to decrease CO_2 emission [5–7]. Various processes for the synthesis of primary amines including direct reaction of ammonia with alkyl halides, reductive amination of carbonyl compounds or alcohols, hydrogenation of nitriles and hydrocyanation of alkenes followed by reduction have been developed [8]. Among them, reductive amination (RA) of Biomass-derived carbonyl compounds with ammonia as a nitrogen source has received increasing attention for producing primary amines, which is an effective route compared to other synthetic processes using specific nitrogen sources with low atomic efficiency. However, directly producing primary amines are difficult because the initially generated amines are more nucleophilic, resulting easily in the formation of by-products of secondary and tertiary amines [9,10]. Developing efficient catalysts for reductive amination of carbonyl compounds remains a challenging goal.

In recent years homogeneous and heterogeneous catalytic methods for obtaining primary amines have been studied [11–17]. Senthamarai et al. [18] used the $RuCl_2(PPh_3)_3$ catalyst to obtain primary benzylic and aliphatic amines starting from carbonyl compounds. The complex of homogeneous Ir and Rh was adopted to catalyze reductive amination of aromatic ketones, but obtaining few primary amines [19]. In order to improve the catalyst separation and reuse, heterogeneous catalysts have been developed recently. Support modified Co-based catalysts were prepared for the amination of 1,2-propanediol and the catalytic activity was related to the catalyst with the special structure derived from the preparation method [20]. Bódis et al. [21] reported carbon-based noble metals (Pt, Pd, Rh, and Ru) catalysts for RA of butyraldehyde with NH_3, and found that the Ru and Rh catalysts were in favor of the formation of primary amine, while the Pt and Pd catalysts were active for the production of secondary amine. The Ru-NP based catalyst was reported for reductive amination of various carbonyl compounds, and the specific flat-shaped morphology and surface electronic structure of Ru NPs were contributed to the catalytic performance [22]. On the other hand, Yan et al. [23] developed an efficient chemical means to produce amino acids from renewable feedstock, in which the designed Ru/CNT catalyst converted glucose into alanine in 43 % yield. Significantly, methanol is identified as an effective solvent for reductive amination of carbonyl

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[24].

Furfurylamine (FAM) known as one of primary amines is a useful compound in preparing drugs, fibers and pesticides. It can be synthesized through reductive amination of its corresponding aldehyde or alcohol over metal catalysts. Recently, the synthesis of furfurylamine from furfuryl alcohol over RANEY® nickel have been reported [25]. Furfuryl alcohols are synthesized by hydrogenation of furfural, it's apparently direct reductive amination of furfural would be a more desirable process. But furfural amination is still rarely explored due to easy hydrogenation of −CHO groups and the ring opening reaction. It has been well known that the activity and selectivity of RA of carbonyl compounds over metal-supported catalysts are influenced obviously by acid sites [26]. The results of Nakamura et al. [27] indicated that Lewis acid sites on the Pt-based catalyst played a critical role in promoting the formation of primary amine for the amination of ketones. Liang et al. [28] reported reductive amination of biomass-derived aldehydes/ketones, and found that RuO_2 provided the strong Lewis acid sites for facilitating the activation of carbonyl groups, while metallic Ru worked as active phase to convert imine to primary amines. Therefore, control of acid sites on metal-based catalysts leads to an efficient role for reductive amination of carbonyl compounds. However, systematic research on the relationship between catalyst acidity and RA performance is still scarce. Zeolite possessed with both the Lewis acid sites and Brönsted acid sites may be used to optimize the catalytic performance of reductive amination, while zeolite modified metal-based catalysts for reductive amination of carbonyl compounds are rarely reported [29].

In this work, HZSM-5 modified Ru-based catalysts with different SiO_2/Al_2O_3 ratios were prepared and applied to the reductive amination of furfural. The synergistic effect between RuO_2 and metallic Ru as well as tuning acid sites of HZSM-5 by changing the SiO_2/Al_2O_3 ratios were further investigated to reveal the structure-performance relationship. In addition, the reaction conditions such as substrate/ammonia ratio, reaction temperature, hydrogen pressure and catalyst amount were studied in detail to optimize the catalytic performance.

2. Experimental section

2.1. Materials

HZSM-5(x) zeolites and S-1(silicalite-1 with MFI zeotype) zeolite were purchased from Nankai University Catalyst Co., Ltd (x represents the ratio of SiO_2/Al_2O_3). Ruthenium trichloride hydrate ($RuCl_3{\cdot}xH_2O$) (35.0–42.0 wt%) was purchased from Aladdin Chemical. 5.0 wt% Ru/C was purchased from TCI Chemical. Furfural (Sinopharm Chemical), furfurylamine (Aladdin Chemical), furfuryl alcohol (Aladdin Chemical), tetrahydrofurfurylamine (Aladdin Chemical), n-heptane (Sinopharm Chemical) were purchased and used as received.

2.2. Catalyst preparation

Ru-supported zeolite catalysts (Ru loading = 5 wt%) were prepared via a wet impregnation method. Typically, the zeolite support was mixed with the solution of $RuCl_3$, and the mixture was slowly evaporated at 60 °C with stirring and dried at 80 °C for 12 h. Then, the as-prepared solid was calcined at 400 °C for 4 h and was reduced at 300 °C for 2 h under H_2 atmosphere, passivated under 2 % O_2/N_2 for 4 h at room temperature. Other supported metal catalysts were also prepared under the same conditions.

2.3. Catalyst characterization

Scanning electron microscopy (SEM; TESCAN MIRA 3 LMH) was used to examine the morphological characteristics of the catalysts. Nitrogen adsorption isotherms were measured at −196 °C using an ASAP 2010 apparatus (Micromeritics). All samples were degassed for 6 h at 200 °C in a nitrogen flow prior to the physisorption measurements.

H_2-TPR and NH_3-TPD were carried out using a multifunctional dynamic adsorption instrument equipped with a TCD detector (DAS-7000 type of Hunan Huasi Instrument Co., Ltd.). 0.05 g of the catalyst was loaded in a quartz tube reactor, and heated in N_2 flow at 350 °C for 1 h with a ramp of 10 °C/min. The sample was cooled down to 50 °C and switched to 5 % H_2/N_2 mixture for reduction. After the baseline was stabilized, the temperature was raised to 800 °C at a ramp of 10 °C/min and the consumption of hydrogen was recorded by TCD. CuO powder was used to calibrate the detector signal. For NH_3-TPD, 0.1 g of the catalyst was loaded and heated in N_2 flow at 350 °C for 2 h, after which the sample was cooled down to 100 °C. The sample was exposed to a 5 % NH_3/N_2 flow for 1 h, and then temperature-programmed desorption was performed up to 800 °C, with a heating ramp of 8 °C/min.

XRD patterns were obtained using a Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation. X-ray photoelectron spectra (XPS) was performed on a Thermo Scientific Escalab 250-X-ray photoelectron spectrometer with Al Kα radiation for the X-ray source. The binding energies of Ru 3p were calibrated by referencing to the C1s line at 284.6 eV.

2.4. General procedure for reductive amination of furfural

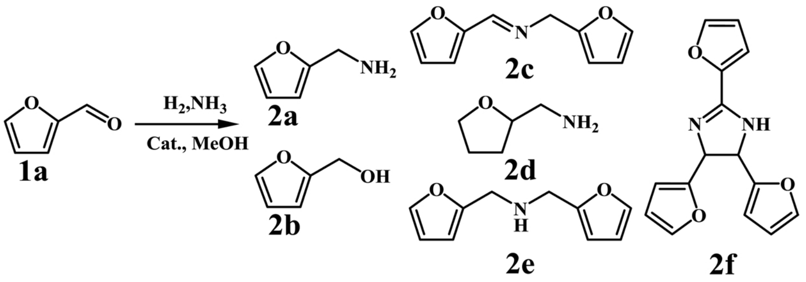
The experiment of the catalysts for reductive amination of furfural was carried out in a stainless-steel 50 ml autoclave equipped with a magnetic stirrer, temperature and pressure control system. In all reactions, the solvent is methanol. Typically, the substrate (2 mmol), catalyst (100 mg) and ammonia solution (6 mL, Aladdin, 7 M in methanol) were charged into the autoclave. The autoclave was closed, flushed with H_2 five times to remove air, and then pure H_2 gas was charged until the pressure of 2.0 MPa. The autoclave was carried out at 80 °C under stirring for 2 h. After the reaction, the autoclave was cooled down in ice-water and then depressurized slowly. The suspension of autoclave was filtered to separate the products. All liquid products were identified by GC–MS. Conversion and yield of products were determined by GC using n-heptane as an internal standard.

3. Results and discussion

3.1. Catalytic performance on reductive amination of furfural

Different potential catalysts were studied for reductive amination of furfural with ammonia solution and H_2 selected as a model reaction, and the results were shown in Table 1. In order to obtain the high yield of furfurylamine, different noble metal catalysts such as Ru, Pt, Pd and Rh supported on HZSM-5 (46, $SiO_2/Al_2O_3 = 46$) were carried out firstly. During the reaction process, furfural is converted to furfurylamine (**2a**) and several byproducts, such as furfuryl alcohol (**2b**), Schiff base N-furfurylidenefurfurylamine (**2c**), tetrahydrofurfurylamine (**2d**), difurfurylamine (**2e**) and 4,5-tris(2-furyl)imidazoline (**2f**). Supported Ru, Pd, Pt and Rh catalysts are tested under similar conditions and obtain **2a** in good to moderate yields (44–76 %). Ru/HZSM-5(46) exhibits the best catalytic performance of furfurylamine (76 % yield of **2a**, entry 1) compared to the Pt, Pd and Rh based catalysts, demonstrating that Ru metal is in favor for the formation of primary amine in contrast to Pt, Pd and Rh metals. In addition, only 4 % of **2b** (entry 4) is detected at the Pt-based catalyst (entry 4), indicating that direct hydrogenation of carbonyl is not the main pathway. Hydrogenation of furan ring is more likely to occur on metal Rh giving a moderate yield of **2d** (34 %, entry 5). Hydrogenation of dimeric imine **2c** to secondary amine **2e** is notable for the Pd-based catalyst (20 %, entry 3), suggesting that the relative rate of hydrogenolysis and hydrogenation for **2c** is mainly depended on active metal species. Especially, compared to Ru/HZSM-5(46), a commercial Ru/C catalyst presents only half the yield of furfurylamine (40 %, entry 2), implying that the combination of Ru and HZSM-5 displays an optimized catalytic performance on the reductive

Table 1
Reductive amination of furfural over supported metal catalysts.[a]



Entry	Catalysts	Con.(%)		Yield (%)				
			2a	2b	2c	2d	2e	2f
1	Ru/HZSM-5(46)	> 99	76	< 1	7	< 1	< 1	8
2	Ru/C	> 99	40	< 1	8	6	< 1	2
3	Pd/HZSM-5(46)	> 99	44	< 1	4	2	20	< 1
4	Pt/HZSM-5(46)	> 99	47	4	1	< 1	5	3
5	Rh/HZSM-5(46)	> 99	49	1	< 1	34	1	2
6[b]	Ru/HZSM-5(27)	> 99	14	< 1	26	< 1	< 1	8
7[b]	Ru/HZSM-5(36)	> 99	22	< 1	17	< 1	< 1	3
8[b]	Ru/HZSM-5(46)	> 99	31	< 1	45	< 1	< 1	9
9[b]	Ru/HZSM-5(81)	> 99	25	< 1	16	< 1	< 1	4
10[b]	Ru/S-1	> 99	17	< 1	24	< 1	< 1	9
11[b]	HZSM-5(46)	98	< 1	< 1	< 1	< 1	< 1	8
12[b]	Blank	> 99	< 1	< 1	< 1	< 1	< 1	12

[a] Reaction conditions: furfural (2 mmol), catalyst (0.15 g), 3 MPa H_2, NH_3 (7 M in MeOH 6 mL), 100 °C,15 min.

[b] Catalyst (0.1 g), 2 MPa H_2, 80 °C, 2 h. The catalysts were labeled as Ru/HZSM-5(x) (x represent the SiO_2/Al_2O_3 ratio).

amination of furfural.

Besides, acid sites of HZSM-5 have an obvious effect on the RA performance of furfural. From Table 1 it is seen that Ru/S-1 with no acid sites displays only 17 % yield of **2a**. As aluminum element is added into the catalyst, the furfurylamine yield increases obviously. A decrease in the SiO_2/Al_2O_3 ratio of HZSM-5 improves the yield of **2a**, and the maximum value is obtained as the SiO_2/Al_2O_3 ratio decreases to 46. As the SiO_2/Al_2O_3 ratio is below 46, the yield of **2a** begins to decrease, indicating that the addition of excess acid sites on HZSM-5 is not beneficial to the formation of furfurylamine (vide infra). In contrast, the blank or single zeolite has no activity to produce furfurylamine (entry 11 and 12). This demonstrates that combining Ru with acidic HZSM-5 together plays a critical role in promoting the formation of furfurylamine.

3.2. *Catalytic characterization of the Ru/HZSM-5 catalysts*

In order to reveal the structure-performance relationship of RA of furfural, numerous techniques were conducted together to characterize microstructures of the Ru/HZSM-5 catalysts with different SiO_2/Al_2O_3 ratios.

The H_2-TPR profile of the Ru/HZSM-5 catalysts with different SiO_2/Al_2O_3 ratios was shown in Fig. 1. There is one reduction peak for Ru/S-1 and Ru/HZSM-5(81), while two reduction peaks for other Ru/HZSM-5 catalysts, respectively. The lower reduction peak at about 170 °C is ascribed to the reduction of surface RuO_2, and the higher reduction peak at about 180 °C is attributed to the reduction of interface RuO_2, in which RuO_2 is probably combined with aluminum in HZSM-5, forming a strong Ru-O-Al bond by sharing the common oxygen atoms [30,31]. Only surface RuO_2 appears for the Ru/S-1 catalyst without the addition of aluminum species. As few aluminum is added into the zeolite (HZSM-5(81)), no interface RuO_2 is observed for the Ru/HZSM-5(81) catalyst, which may be attributed to the weakened combination between RuO_2 and aluminum, restraining the formation of interface RuO_2. As the SiO_2/Al_2O_3 ratio decreases continually to 46, the reduction peak of interface RuO_2 appears, implying that the interaction of RuO_2 and Al in HZSM-5 is strengthened, resulting in the formation of the Ru-O-Al bond. Besides, the reduction peak of interface RuO_2 shifts gradually towards higher temperature with the decrease of SiO_2/Al_2O_3 ratio, suggesting that the Ru-O-Al bond in the Ru/HZSM-5 catalyst is enhanced in the lower SiO_2/Al_2O_3 ratio. In addition, the reduction degree of Ru species over all of the Ru/HZSM-5 catalysts calculated from H_2-TPR is 73.8–81.7 % (Table S1). In contrast, the Ru/S-1 catalyst displays a lower reduction degree of 64.5 % for Ru species, which may be one of the reasons for the poor catalytic performance of Ru/S-1.

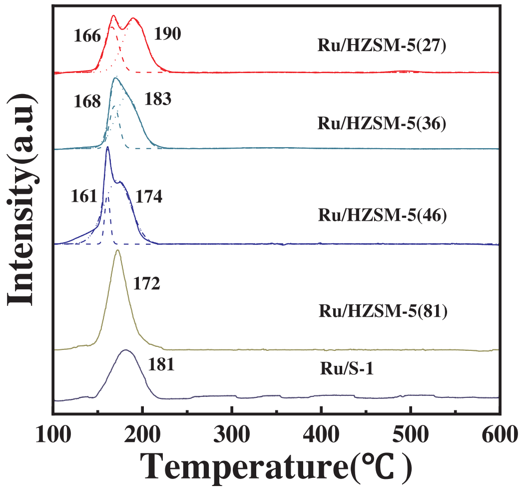


Fig. 1. H_2-TPR profile of the different catalysts.

Such interaction between Ru metal and HZSM-5 was also found in NH_3-TPD, as shown in Fig. 2. No peaks of acid sites is observed for S-1. All of the HZSM-5 zeolites with different SiO_2/Al_2O_3 ratios display two peaks at about 280 and 460 °C, which are attributed to the weak and strong acid sites with framework Al, respectively [32]. The intensity of both the weak and strong acid sites presents an increasing trend with the decrease of SiO_2/Al_2O_3 ratio from 81 to 27. The value of total

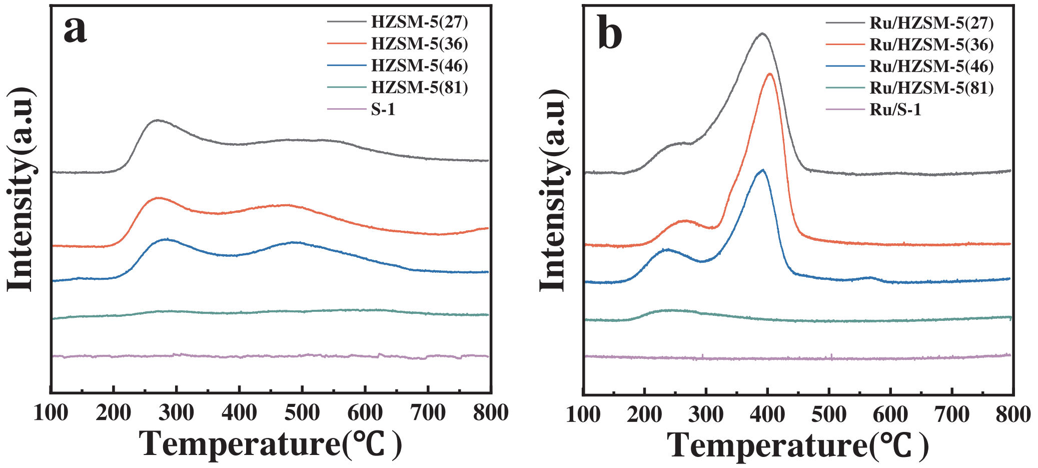


Fig. 2. (a) NH_3-TPD profile of catalysts without Ru loading (b) NH_3-TPD for catalysts after Ru loading.

Table 2
Amount and type of acid sites as determined by NH_3-TPD.

	Catalyst	Low Temperature Peaks (°C)	Amount of weak acid sites (mmol/g)	High Temperature Peaks (°C)	Amount of strong acid sites (mmol/g)	Total acidity (mmol/g)
1	HZSM-5(27)	280	0.092	465	0.219	0.311
2	HZSM-5(36)	274	0.077	444	0.207	0.284
3	HZSM-5(46)	288	0.079	483	0.170	0.249
4	HZSM-5(81)	291	0.012	540	0.030	0.042
5	S-1	–	–	–	–	–
6	Ru/HZSM-5(27)	258	0.089	382	0.335	0.424
7	Ru/HZSM-5(36)	266	0.065	395	0.292	0.357
8	Ru/HZSM-5(46)	243	0.077	382	0.182	0.259
9	Ru/HZSM-5(81)	256	0.029	384	0.005	0.034
10	Ru/S-1	–	–	–	–	–

acidity increases from 0.042 mmol/g of HZSM-5(81) to 0.311 mmol/g of HZSM-5(27), as listed in Table 2. After the introduction of Ru species into the zeolites, the peak of strong acid sites approximately reduces to 385 °C accompanied by a significant enhancement of intensity. The enhancement of strong acid sites may be attributed to the interface RuO_2 forming by the strong interaction between Ru and aluminum, which is more obvious as the aluminum content increases. Taking Ru/HZSM-5(27) as a sample, the amount of strong acid sites increases by 53 % after the loading of Ru into HZSM-5(27). Additionally, the total acid sites content of Ru/HZSM-5(81) is 0.034 mmol/g, which increases gradually to 0.424 mmol/g of Ru/HZSM-5(27) as the SiO_2/Al_2O_3 ratio decreases from 81 to 27. The experiment results mentioned above indicate that the yield of **2a** increases firstly with the decreasing SiO_2/Al_2O_3 ratio, and then reaches the maximum value at the SiO_2/Al_2O_3 ratio of 46. Further decrease in SiO_2/Al_2O_3 ratio results in the decrease of the **2a** yield. Meanwhile, the amount of acid sites and the Ru-O-Al bond force present an increasing trend with the decrease in the SiO_2/Al_2O_3 ratio. Therefore, it is considered that the Ru/HZSM-5(46) catalyst with modified acid sites and interaction of metal-support has the optimized catalytic performance for RA of furfural.

The textural properties of the Ru/HZSM-5 catalysts were summarized in Table 3. It is found that the Ru/HZSM-5 catalysts with different SiO_2/Al_2O_3 ratios show comparable surface areas of approximately $273 - 315\ m^2/g$ with micropores of approximately 0.37 nm and mesopores of 2.6–4.0 nm. In contrast, Ru/S-1 presents the maximum value of BET surface area (315 m^2/g) and the minimum value of mesopores (2.2 nm), indicating that the S-1 support is more favorable to the dispersion of Ru species on the surface layers. Especially, the results of H_2-TPD shown in Table S2 indicate that the dispersion degrees of Ru species are in the range of 8.7–24.7 %, and the average Ru nanoparticles sizes are between 4.1–11.7 nm for the Ru/HZSM-5 catalysts, while Ru/S-1 displays the largest dispersion (29.6 %) and smallest particle size (3.4 nm), further confirming the excellent dispersion ability of S-1. Synchronously, Ru/S-1 has no acid sites, which displays the poor catalytic performance in comparison to the Ru/HZSM-5 catalysts with acid sites, suggesting that the dispersion of Ru nanoparticles has a negligible role whereas acid sites of the Ru/HZSM-5 catalysts play a critical role in promoting the reductive amination of furfural.

The micro-structures of Ru/HZSM-5(46) were further analyzed. Fig. 3 showed the SEM micrograph and EDS mapping of the Ru/HZSM-5(46) catalyst. It is apparent that a normal zeolite morphology is displayed for the HZSM-5 support [33], and Ru species are well dispersed on the surface of HZSM-5. The microstructures of Ru/HZSM-5(46) were characterized by XRD and XPS, respectively. From Fig. 4a it is found that HZSM-5 is composed of the MFI structure, and adding Ru metal into zeolite does not change the MFI structure of HZSM-5. Ru species exists in the RuO_2 form on the surface of fresh Ru/HZSM-5(46) catalyst. After reduction and reaction, new diffraction peaks of Ru metal appear at 38.4° (100) and 44.0° (101), indicating that part of RuO_2 species have been converted to metallic Ru during the reduction and reaction. Especially, the MFI structure of HZSM-5 remains unchanged in this process. The results of XPS (Fig. 4b) show that the diffraction peaks at 462.2 eV and 463.5 eV are observed on the surface of reduced Ru/HZSM-5(46), which are ascribed to Ru (0) and RuO_2, respectively, confirming that RuO_2 species on the surface of HZSM-5 are converted partially to metallic Ru species during reduction. The reduction degree of Ru species was calculated to be 77.3 % from XPS, which is consistent with the value from the H_2-TPR (Table S1, 78.4 %) and ensured that the catalyst will not be further oxidized in the atmosphere. The results of Liang et al. indicated that RuO_2 provided the Lewis acid sites for promoting the activation of carbonyl groups, whereas metallic Ru facilitated the hydrogenation of imine [28]. In the present study, both the

Table 3
Physicochemical properties of the Ru/HZSM-5 catalysts.

Entry	Catalyst	S_{BET} [a] (m^2/g)	V_{mic} [b] (cm^3/g)	D_{mic} [b] (nm)	V_{meso} [c] (cm^3/g)	D_{meso} [d] (nm)
1	Ru/HZSM-5(27)	316	0.14	0.37	0.08	3.78
2	Ru/HZSM-5(36)	315	0.14	0.38	0.07	3.85
3	Ru/HZSM-5(46)	273	0.12	0.37	0.08	3.99
4	Ru/HZSM-5(81)	295	0.12	0.34	0.14	2.60
5	Ru/S-1	350	0.15	0.36	0.11	2.23

[a] Determined by BET method.
[b] Determined by Horvath-Kawazoe method.
[c] $V_{meso} = V_{total} - V_{mic}$.
[d] Determined by BJH method from the desorption branch of the isotherm curves.

RuO_2 and metallic Ru species commonly exist in the Ru/HZSM-5(46) catalyst during reaction. It is possible that synergistic effect between RuO_2 and metallic Ru strengthens the reductive amination of furfural, promoting the formation of furfurylamine compared to Pt, Pd and Rh supported on the HZSM-5 catalysts.

3.3. Optimization of the reaction conditions

Ru/HZSM-5(46) was proved as an efficient catalyst for producing selectively furfurylamine in the reductive amination of furfural. Subsequently, the effect of reaction conditions including substrate/ammonia ratio, reaction temperature, hydrogen pressure and catalyst amount were further investigated over Ru/HZSM-5(46). Fig. 5a showed the effect of the substrate/ammonia ratio on product distribution. Adjustment of substrate/ammonia ratio may change the selectivity of furfurylamine because reductive amination of the −CHO group could be changed via adding ammonia. From Fig. 5a it can be seen that a decrease in the substrate/ammonia ratio increases the yield of furfurylamine and displays the maximum yield of 32 % as the substrate/ammonia ratio reaches 0.05. A further increase in the ammonia content inhibits the formation of furfurylamine, whereas increases the yield of Schiff base N-furfurylidenefurfurylamine, indicating that excess ammonia may facilitate the conversion of furfurylamine and furfural, promoting the formation of Schiff base type intermediates. Therefore, tuning the ratio of substrate/ammonia to 0.05 achieves the maximum yield of furfurylamine under the existed reaction conditions.

The effect of reaction temperature on the performance of reductive amination of furfural was investigated in the temperature range of 40–120 °C (Fig. 5b). A low temperature of 40 °C results in the formation of Schiff base type intermediates composed mainly of **2c** and **2f** (~52 % of yield), whereas no formation of furfurylamine is observed. A slight increase of temperature to 60 °C increases distinctly the yield of Schiff base type intermediates. Further increasing reaction temperature results in the formation of furfurylamine, the amount of which reaches a maximum of 49 % at 100 °C accompanied by the decrease in Schiff base type intermediates. It is possible that the reductive amination of furfural promotes firstly the formation of Schiff base type intermediates, which is converted continually to furfurylamine via hydrogenolysis or hydrogenation [34]. The temperature below 60 °C is insufficient for producing furfurylamine. Further increase in the temperature above 100 °C leads to a decrease in the yield of furfurylamine, which may be attributed to the formation of unidentified products.

Fig. 5c showed the catalytic performance of Ru/HZSM-5(46) with various hydrogen pressure. A low hydrogen pressure of 0.5 MPa results in the formation of 16 % yield of **2a**, and 40 % yield of Schiff base type intermediates (**2c** and **2f**). No formation of imine is observed in this

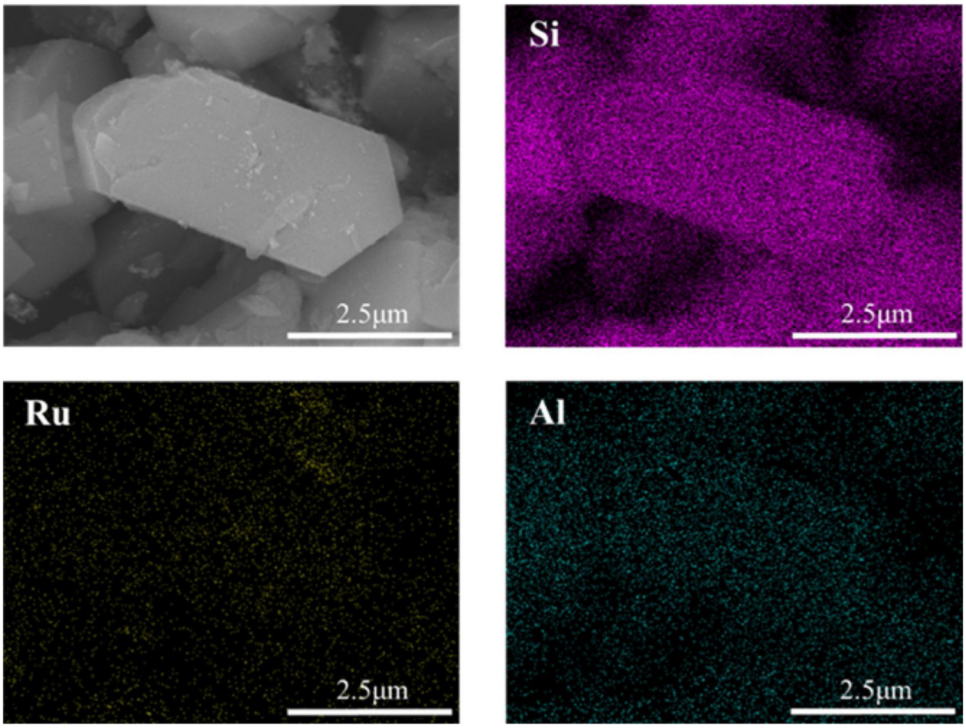


Fig. 3. SEM micrograph and EDS mapping of Ru/HZSM-5(46) catalyst showing the elemental distributions of Si, Al and Ru.

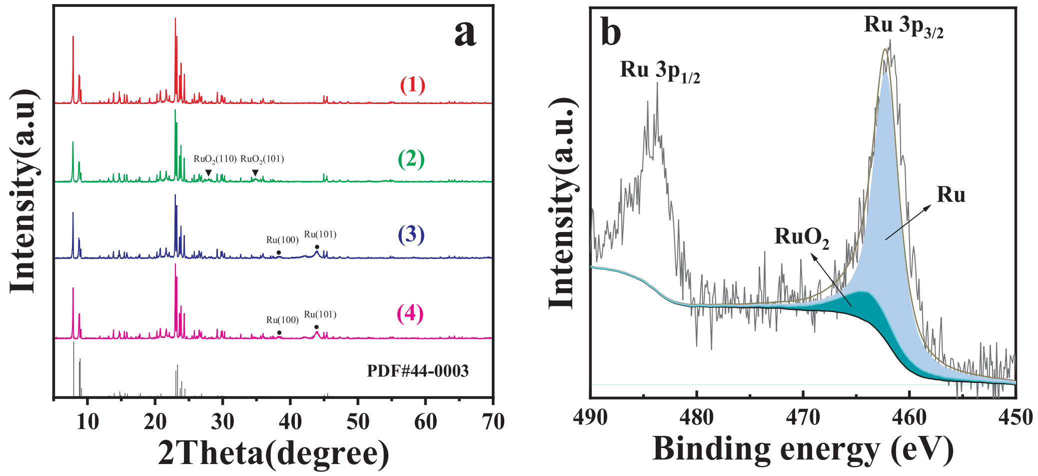


Fig. 4. (a) XRD pattern of the (1) ZSM-5(46), (2) calcined Ru/ZSM-5(46), (3) Ru/ZSM-5(46) after reduction, and (4) Ru/ZSM-5(46) after reaction (b) Ru 3p XPS spectra of reduced Ru/HZSM-5(46).

process, which may be attributed to rapid conversion of imine to furfurylamine in the initial stage under H_2 atmosphere [35]. With the increase of H_2 pressure, the yield of furfurylamine increases gradually, accompanied by a decrease of the yield to **2c**. The highest yield to **2a** is 67 % when hydrogen pressure is 3 MPa and 3 % yield of tetrahydrofurfurylamine **2d** is observed in this condition. Further increase in the hydrogen pressure to 4 MPa does not change the yield of **2a**, while the yield of **2d** increases to 5 %, suggesting higher hydrogen pressure is conducive to the hydrogenation of furan ring.

The effect of the catalyst amount on the performance of reductive amination of furfural was shown in Fig. 5d. The furfurylamine yield increases gradually with an increasing Ru/HZSM-5(46) amount and

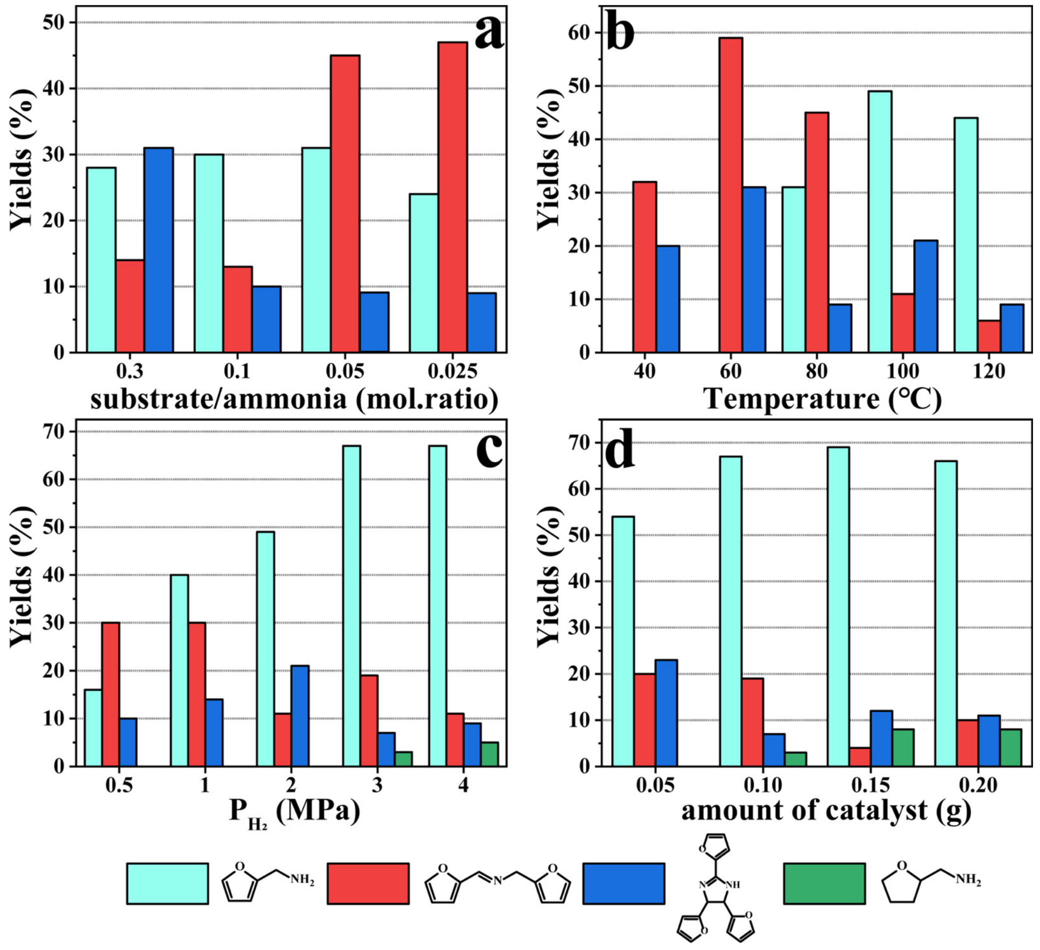


Fig. 5. (a) Effect of substrate/ammonia ratios on product distribution for the reductive amination of furfural. Reaction conditions: furfural (2 mmol), catalyst (0.1 g), 2 MPa H_2, 80 °C, 2 h. (b) Effect of temperature on product distribution for the reductive amination of furfural. (c) Effect of hydrogen pressure on product distribution for the reductive amination of furfural. Reaction conditions: 100℃. (d) Effect of substrate/catalyst ratio on product distribution for the reductive amination of furfural. Reaction conditions: 3 MPa H_2.

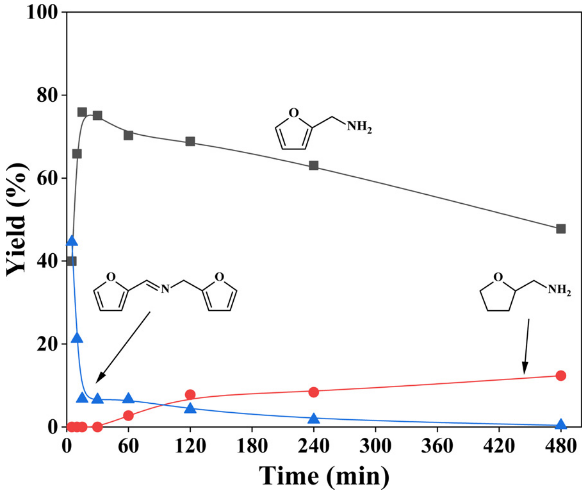


Fig. 6. Time courses for the reductive amination of furfural. Reaction conditions: furfural (2 mmol), catalyst (0.15 g), 3 MPa H_2, NH_3 (7 M in MeOH 6 mL), 100 °C.

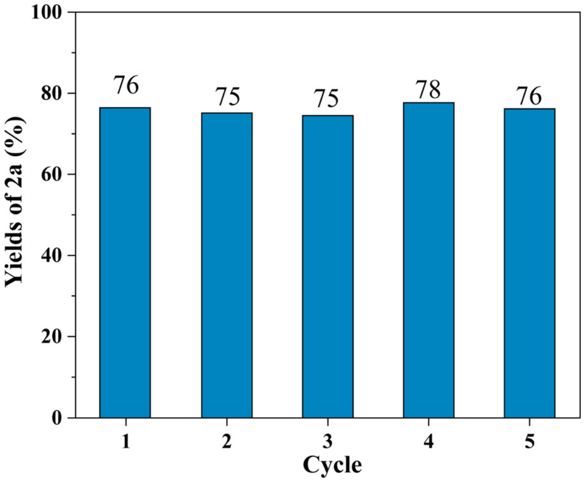


Fig. 7. Reuse experiments of Ru/ZSM-5(46) catalyst for the reductive amination of furfural. Reaction conditions: furfural (2 mmol), catalyst (0.15 g), 3 MPa H_2, NH_3 (7 M in MeOH 6 mL), 100 °C, 15 min.

reaches a maximum of 68 % at 0.15 g catalyst loading. Further increase in the catalyst loading results in the decrease of the furfurylamine yield, which implies that a moderate amount of catalyst is necessary to promote the reductive amination of furfural.

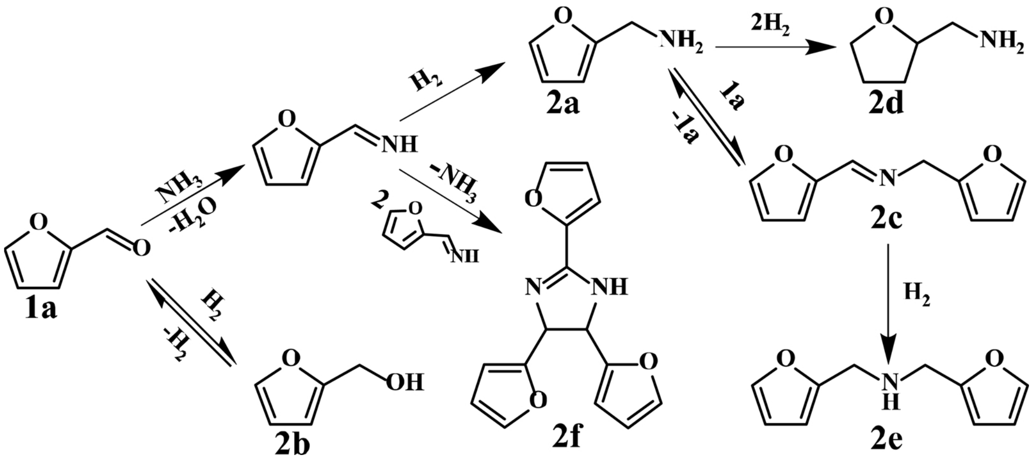
3.4. Probable reaction pathways

In order to explain the reaction pathway of the formation of furfurylamine, the distribution of furfural reductive amination products by varying the reaction time using Ru/HZSM-5(46) was shown in Fig. 6. All substrates are converted within the reaction time of 5 min, which means the reaction between furfural and ammonia happens rapidly. The highest yield of **2a** is quickly achieved as the yield of **2c** decreases rapidly at the reaction time of 15 min, suggesting that **2c** is the key intermediate. There is a pathway for **2c** converting to **2a**, which is consistent with the previous reports [10,35,36]. As the reaction time continues, both the yields of **2a** and **2c** present a decreasing trend while that of **2d** increases slightly, implying that the hydrogenation of furan ring takes place with time on stream. The yield of **2f** increases gradually with time on stream, and remains at 12 % (Table S3) after 15 min without converting to other products.

Based on the above results probable reaction pathways were shown in Scheme 1. Initially, the reaction of **1a** with NH_3 results in the formation of imines, which are unable to be detected because of the poor stability of imines. In the blank or single HZSM-5 (Table 1, entry 11 and 12), imines are only converted to **2f**, suggesting that the formation of **2f** may not be a catalytic process. As Ru is combined with HZSM-5, imines are reduced to **2a.** Due to more nucleophilic of **2a** than ammonia, **2a** can react preferentially with **1a** to form Schiff base **2c**. The Schiff base may further reduce to **2e** by hydrogenation or hydrogenolysis to form **2a**. The selectivity between **2a** and **2e** is depended on the relative rate of hydrogenolysis and hydrogenation. On the other hand, the over-hydrogenation of furan ring on **2a** causes easily the formation of **2d.** Liu et al. [25] reported the reductive amination of furfuryl alcohol **2b** to furfurylamine **2a,** and dehydrogenation of **2b** to **1a**. Inspired by **2b** detected in our products, we believe that there may be a reversible transformation between **1a** and **2b** in the reaction.

3.5. Recycle study of the catalyst

The possibility of recovery and reusability of Ru/HZSM-5(46) were studied through the reuse experiments. After the reaction, the mixture is centrifuged and filtered to separate the catalyst. The catalyst is washed with water and ethanol for several times, dried at 60 °C for 10 h. The Ru/HZSM-5(46) catalyst is used for five times and noticeable decrease in **2a** yield is not observed (Fig. 7). Furthermore, no apparent difference is found in XRD patterns (Fig. 4a), indicating that Ru/HZSM-5(46) is stable and used as a reusable catalyst for the reductive amination of furfural.



Scheme 1. A possible reaction path of the formation of furfurylamine under the studied reaction conditions.

4. Conclusions

In summary, we performed the reductive amination of furfural over the Ru/HZSM-5 catalysts with different SiO_2/Al_2O_3 ratios. The strong interaction between ruthenium and aluminum increased the acid sites of Ru/HZSM-5, affecting obviously the product distribution. Both the RuO_2 and metallic Ru species were existed commonly for the Ru/HZSM-5 catalyst, synergistic effect of which enhanced the reductive amination of furfural compared to other noble metals such as Pt, Pd and Rh. The Ru/HZSM-5(46) catalyst with modified acid sites and interaction of the Ru-O-Al bond displayed the optimized catalytic performance for producing furfurylamine. Under the optimized conditions, the highest yield of 76 % to furfurylamine was achieved after the reaction only 15 min and the catalyst could be recycled five times without loss of performance. These findings suggest that Ru/HZSM-5 is a potentially very attractive catalyst for the conversion of furfural to furfurylamine, which displays a potential pathway for further industrial applications.

CRediT authorship contribution statement

Chenglong Dong: Conceptualization, Methodology, Writing - original draft, Investigation. **Hongtao Wang:** Methodology. **Haochen Du:** Investigation. **Jiebang Peng:** Investigation. **Yang Cai:** Investigation. **Shuai Guo:** Data curation. **Jianli Zhang:** Resources. **Chanatip Samart:** Resources. **Mingyue Ding:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110755.

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