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Short Communication

The reductive amination of cyclohexanone with 1,6-diaminohexane over alumina B modified Cu–Cr–La/γ-Al_2O_3

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ABSTRACT

The reductive amination of cyclohexanone with 1,6-diaminohexane over alumina B modified Cu–Cr–La/γ-Al_2O_3 was investigated. The experimental results indicated that the doped alumina B remarkably increased the selectivity of N, N′-dicyclohexyl-1,6-diaminohexane. The catalysts were studied by BET, XRD, TEM and NH_3-TPD, the introduction of alumina B to Cu–Cr–La/γ-Al_2O_3 reduced the strong acid capacity of the catalyst, which inhibited the generation of cyclohexane and 2-cyclohexylidene-cyclohexanone, and facilitated the desorption of amino compounds. The reaction parameters, including reaction temperature and molar ratio of starting materials, were optimized and a 92.6% selectivity of N, N′-dicyclohexyl-1,6-diaminohexane was obtained under optimized conditions.

1. Introduction

Secondary amines are a key class of intermediates of industrial chemicals [1–3]. One of the most useful methods for the preparation of secondary amines is the reductive amination of aldehydes or ketones with primary amines in the presence of hydrogen and a heterogeneous metal catalyst [4–11], and all these works are about the reductive amination of carbonyl compound with monoamine. In industry, the reductive amination of carbonyl compound with primary diamine, such as 1,6-diaminohexane, was rarely reported and suffered from low selectivity of N, N′-dicyclohexyl-1,6-diaminohexane and tedious process [12–14]. Thus an attempt was made to establish a continuous process for the reductive amination of cyclohexanone with 1,6-diaminohexane.

Since Cu–Cr–La/γ-Al_2O_3 was developed and demonstrated to be effective for the reductive amination of triacetoneamine with *n*-butylamine in our previous work [15], it thus was first employed for the reaction of cyclohexanone with 1,6-diaminohexane. In this work, in order to reduce the acidic centers of catalyst, the alumina B (basic alumina, pH > 8) was added to the Cu–Cr–La/γ-Al_2O_3 and the obtained catalysts were applied to this reaction. The modified catalysts were studied by XRD and NH_3-TPD, and the reaction parameters were also investigated.

2. Experimental

2.1. Materials and catalysts

All the chemicals were reagent grade and were used without further purification. The $Cu_{20}Cr_5La_5$/γ-Al_2O_3-AB_m (AB: alumina B, m: content of alumina B in the catalyst) was prepared by kneading the metal carbonates with the mixture of pseudo-boehmite and alumina B. The detailed procedures for the preparation of metal carbonates and the catalyst were described in our previous work [15]. Take $Cu_{20}Cr_5La_5$/γ-Al_2O_3-AB_{35} (the content of alumina B in the catalyst was 35 wt.%) as an example, 18.24 g dried metal carbonates were kneaded sufficiently with a mixture of 16.54 g pseudo-boehmite and 10.50 g alumina B, accompanied with deionized water as adhesive, followed by molding to bars by an extruder. After dried in air for 6 h at 110 °C, the bars were calcined for 4 h at 500 °C and reduced at 220 °C in a hydrogen stream (1.0 MPa) for 4 h before use.

2.2. Catalysts characterization

The specific surface area was determined by the BET method with N_2 adsorption–desorption measurements at liquid nitrogen temperature using a NOVA 2000e analyzer (Quantachrome, US). X-ray diffraction (XRD) was carried out on a Rigaka D/max 2500 X-ray diffractometer with Cu–K_α radiation (40 kV, 100 mA) in the range of 5–95°. The mean diameter of Cu crystals was calculated from XRD patterns using Scherrer equation. Transmission electron microscopic measurements (TEM) were carried out using a JEOL electron

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microscope (JEM-2010), with an accelerating voltage of 200 keV. NH_3-temperature programmed desorption (NH_3-TPD) was performed with a TP-5000 instrument with a thermal conductivity detector (TCD).

2.3. Catalytic reductive amination

The reductive amination of cyclohexanone with 1,6-diaminohexane was carried out in a tubular, fixed-bed reactor with an inner diameter of 15 mm and a length of 660 mm, which was loaded with 40.0 mL catalysts. A solution of cyclohexanone and 1,6-diaminohexane in 1,4-dioxane was stirred for 10 h at ambient temperature, and then dosed into the reactor at a flow rate of 0.2 mL/min by a syringe pump. The GC–MS (Polaris Q, Thermo Finngan, America) used to confirm the components of the reaction mixture was performed on a HP-5 capillary column (30 m × 0.25 mm, 0.2 μm film thickness) equipped with an ion trap MS detector. The composition of the reaction mixture was determined by GC with a 30 m SE-54 capillary column.

3. Results and discussion

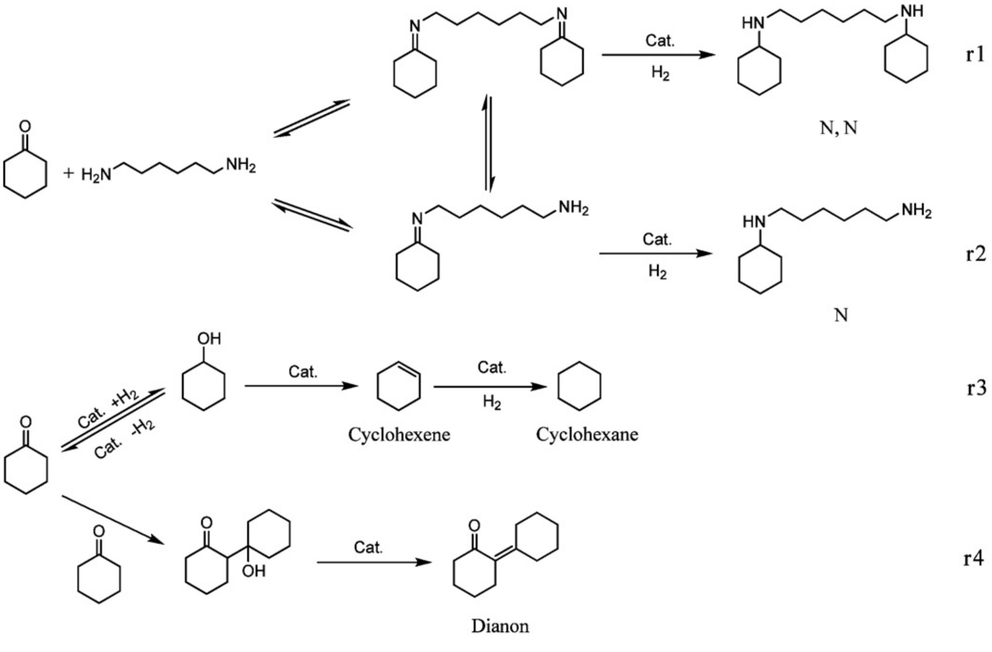
3.1. Catalyst modification

As what mentioned before, Cu–Cr–La/γ-Al_2O_3 was employed for the reaction of cyclohexanone with 1,6-diaminohexane and expected a high yield of N, N′-dicyclohexyl-1,6-diaminohexane. The first 15 h reaction mixture was collected and detected, unexpectedly, only 1,4-dioxane was obtained with this catalyst. We inferred that the amino compounds were possibly adsorbed tightly on the surface of catalyst due to the strong base–acid interreaction between amino compounds and catalyst. However, the similar phenomenon was not observed in the reductive amination of triacetoneamine with n-butylamine over Cu–Cr–La/γ-Al_2O_3. The relatively weak interreaction of monoamine and catalyst than that between diamine and catalyst, and the steric hindrance of amino group in N-butyl-2,2,6,6-tetramethyl-4-piperidinamine were the reasons why the product could be obtained smoothly.

The reaction resultants were flushed out from the catalyst bed by large amount of 1,4-dioxane, and the obtained solution was determined by GC–MS. N, N′-dicyclohexyl-1,6-diaminohexane, the desired product, was detected as the main product. N-cyclohexyl-1,6-diaminohexane (N), cyclohexane and 2-cyclohexylidene-cyclohexanone (Dianon) were detected as major by-products. According to the above results, the reaction pathway was deduced and shown in Scheme 1. N-cyclohexyl-1,6-diaminohexane was reasonably obtained by the reductive amination of 1,6-diaminohexane with 1 eq cyclohexanone (r2). Cyclohexane was considered to be generated from the hydrogenation–dehydration–hydrogenation of cyclohexanone (r3). Dianon could be formed from the aldol condensation of cyclohexanone itself (r4). Chary et al. [16] and Reichle [17] have reported that the strong acidic sites are responsible for cyclohexanol dehydration and cyclohexanone condensation. Additionally, it was also reported that strong acidic sites restraint the desorption of amino compounds from the surface of catalyst [18], and that may be the reason why only solvent was detected in the first 15 h reaction mixture. Thus, even Cu–Cr–La/γ-Al_2O_3 was proved effective for the reductive amination of triacetoneamine with *n*-butylamine, it also should be improved for the reaction of cyclohexanone with 1,6-diaminohexane.

According to the analysis of the above, the strong acid sites on the surface of catalyst were confirmed responsible for the side reactions. Thus, the alumina B was chosen to add to the Cu–Cr–La/γ-Al_2O_3 to decrease the catalyst acidity and the prepared catalysts were employed to the reductive amination of cyclohexanone with 1,6-diaminohexane, and the results are shown in Table 1.

All catalysts exhibited satisfied conversion of cyclohexanone, which means the conversion was completely depending on the metal components but not the support. With the addition of alumina B, the selectivity of N, N′-dicyclohexyl-1,6-diaminohexane increased from 53.1% to 79.1% and thereafter it decreased slightly. There was no cyclohexane and dianon detected when the content of alumina B reached to 50%, the reason is that the low acidity of catalysts can inhibit the dehydration of cyclohexanol and the aldol condensation of cyclohexanone. Nevertheless, the selectivity of N-cyclohexyl-1,6-diaminohexane almost showed no change with the addition of alumina B, which indicated that N-cyclohexyl-1,6-diaminohexane selectivity was impacted mainly by reaction conditions. In addition, all the



Scheme 1. The main and side reaction processes for the reductive amination.

Table 1
Reductive amination of cyclohexanone with 1,6-diaminohexane over various catalysts.

Catalyst	Conversion/%	Selectivity/%				
		Cyclo-hexanol	Cyclo-hexane	Dianon	N[a]	N, N[b]
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$	99.8	17.3	8.2	7.3	14.1	53.1
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{17.5}$[c]	99.8	11.7	4.7	2.4	12.8	68.4
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$	100	8.1	0	0	12.8	79.1
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{52.5}$	100	7.9	0	0	13.6	78.5

Reaction conditions: temperature = 120 °C; hydrogen pressure = 4.0 MPa; flow rate = 0.2 mL/min; cyclohexanone: 1,6-diaminohexane (mole) = 2:1; concentration in 1,4-dioxane = 20.0 wt.%.

[a] N N-cyclohexyl-1,6-diaminohexane.

[b] N, N N, N′-dicyclohexyl-1,6-diaminohexane.

[c] AB alumina B.

Table 2
BET results for the prepared catalysts.

Catalyst	Surface area (m^2/g)	Average pore diameter (Å)	Total pore volume (cm^3/g)
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$	200.0	81.27	0.31
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{17.5}$	208.7	87.23	0.37
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$	224.5	103.10	0.42
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{52.5}$	233.9	108.70	0.52

components could be detected in the first 3 h reaction mixture in case of $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$ and $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{52.5}$. To better understand the effects of alumina B to $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$, the catalysts were characterized by XRD and NH_3-TPD.

3.2. Catalysts characterization

3.2.1. Textural properties of catalysts

The specific surface areas and pore structural parameters of all the four catalysts are summarized in Table 2. As can be seen, the surface area of $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$ is smaller than that of modified by alumina B but the surface areas are still in the similar range due to the small changes. As for the modified catalysts, the surface area, average pore diameter and total pore volume increase with the increase of alumina B amount in the prepared catalysts.

3.2.2. XRD

The XRD curves for the reduced $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$, $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{17.5}$, $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$ and $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{52.5}$ are shown in Fig. 1. The typical diffraction lines at 43.3°, 50.4°, 74.2° and 90.0° in the XRD curves could be assigned to the crystals of elementary copper. There was no evidence for the copper crystalline was affected by the addition of alumina B. Moreover, calculation from the main diffraction line (43.3°) on the XRD patterns using Scherrer equation, the mean diameters of Cu^0 particle in all these four catalysts showed no obvious difference. These results demonstrated that the doped alumina B had no influence to the active species. Furthermore, no obvious peaks corresponding to Cr, La or any their combinations were picked out from the XRD curves, we suggest that these components are either too small to be detected or in the amorphous phases.

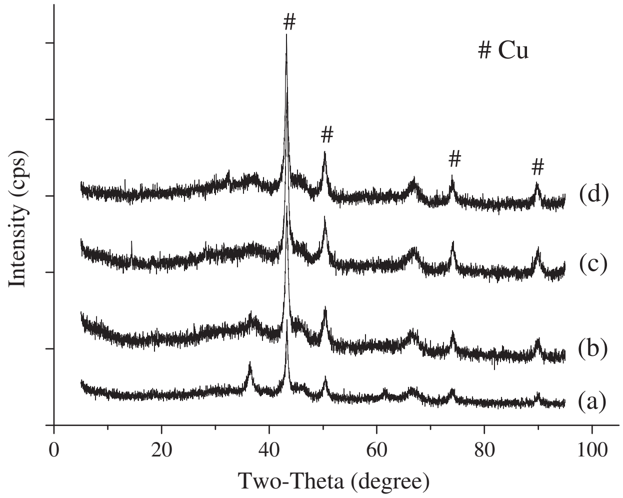


Fig.1. XRD curves for reduced (a) $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$, (b) $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{17.5}$, (c) $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$ and (d) $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{52.5}$.

3.2.3. TEM

TEM images for $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$ and $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$ are shown in Fig. 2. The images showed that the size distribution of copper particles was similar in the both samples. The dispersion and average size of copper particles in $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$ were not so far different from that of $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$, and the structural properties of active species was not influenced by the addition of alumina B, which agreed well with the XRD results.

3.2.4. NH_3-TPD

In the present investigation, NH_3-TPD is used to compare the acidity distinction between $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$ and $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$ and the TPD curves are shown in Fig. 3. The $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$ catalyst exhibited a typical double-peak. The two desorption peaks at the lower temperature (229 °C) and the higher temperature (470–529 °C) correspond to the weak and strong acid sites on the catalyst surface, respectively. As for $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$, the higher temperature peak could not be observed obviously. We deduced that the alumina B neutralized the strong acid sites on the catalyst surface. Furthermore, the area of a specific peak can be used to estimate the amount of ammonia desorbed from the sample, and can be taken as a standard to quantify the acidity of the sample [19,20]. The peak areas for the two catalysts are listed in Table 3, it can be found that the total peak area decreased from 5499 in curve (a) to 2421 in curve (b). Combination with the both points, it is clearly that the addition of alumina B dramatically decreased the acidity of $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$. As shown in Table 1, the selectivity of cyclohexane and dianon decreased from 8.2% and 7.3% to 4.7% and 2.4% with the addition of alumina B, and no cyclohexane and dianon was detected when the content of alumina B reached to 50%. It means that the addition of alumina B to $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$ can decrease the selectivity of cyclohexane and dianon, namely, the lower acidity is responsible for inhibiting the dehydration of cyclohexanol and aldol condensation of cyclohexanone. What's more, all the components could be detected in the first 3 h reaction mixture in case of $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$, which indicates that the low acidity is the reason why the products could be desorbed easily from $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$.

3.3. The effect of reaction temperature

The effect of reaction temperature on the reductive amination of cyclohexanone with 1,6-diaminohexane over $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$

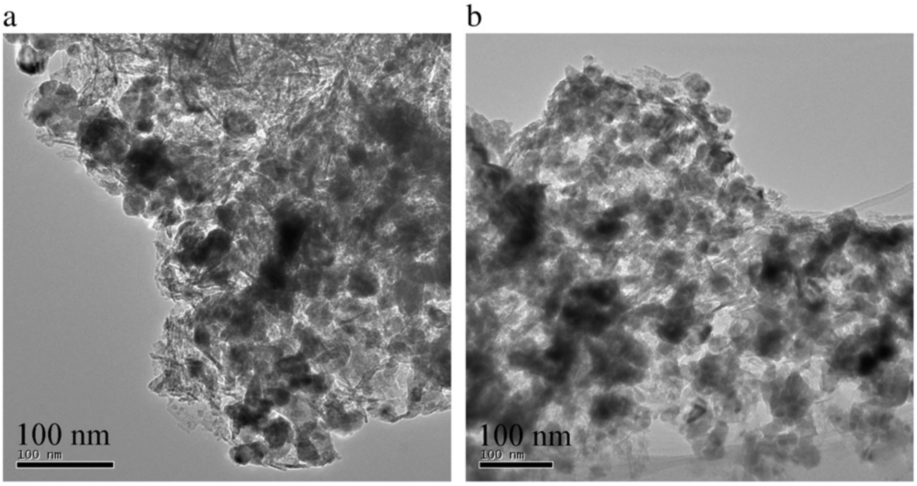


Fig. 2. TEM images for (a) $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$ and (b) $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$.

was investigated and the results are shown in Fig. 4. As can be seen, the conversion of cyclohexanone was independent on the temperature in the range 120 °C–210 °C and remained around 100%. In response to the growing temperature, the selectivity of N, N′-dicyclohexyl-1,6-diaminohexane slightly increased and a highest selectivity of 88.3% was achieved at 180 °C, and thereafter decreased to 75.3% at 210 °C, while the selectivity to cyclohexanol decreased insistently. The reason for the results was deduced. The hydrogenation of cyclohexanone on the surface of catalyst was irreversible at low temperature but reversible at higher temperature (r3 in Scheme 1). At low temperature (≤120 °C), cyclohexanol was generated from the hydrogenation of cyclohexanone and followed by dehydration-hydrogenation to form cyclohexane. However, at the higher temperature (≥150 °C), the dehydrogenation of generated cyclohexanol to cyclohexanone preferentially occurred, and this part of cyclohexanone can further react with 1,6-diaminohexane to form N, N′-dicyclohexyl-1,6-diaminohexane. The similar phenomena were also reported in some other studies [21–24]. Thus, higher temperature was favorable for the production of N, N′-dicyclohexyl-1,6-diaminohexane, but more N-cyclohexyl-1,6-diaminohexane was generated in the temperature range 180 °C–210 °C, 180 °C was chosen as the reaction temperature.

3.4. The effect of molar ratio of starting materials

Due to the unavoidable consumption of cyclohexanone in catalytic hydrogenation and the generation of N-cyclohexyl-1,6-diaminohexane, the appropriate excessive cyclohexanone was considered necessary. Thus, the molar ratio of cyclohexanone to 1,6-diaminohexane over $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$ was studied and the results are shown in Fig. 5. With the molar ratio increased from 2.0 to 2.2, the selectivity of N, N′-dicyclohexyl-1,6-diaminohexane slightly increased from 88.3% to 92.6%. With the further increase in molar ratio, the side reactions increased, and the selectivity of N, N′-dicyclohexyl-1,6-diaminohexane

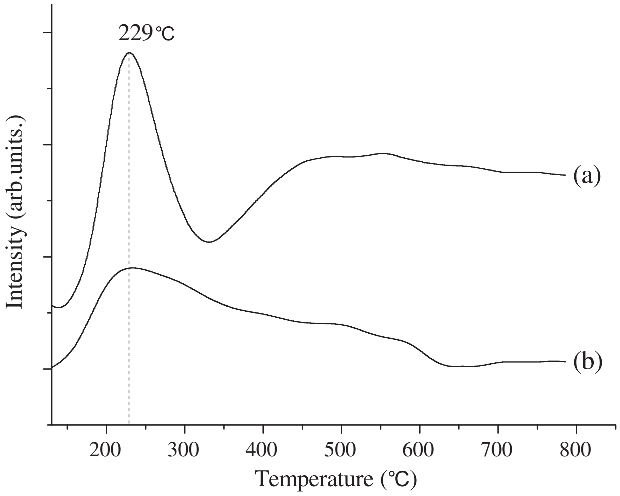


Fig. 3. NH_3-TPD curves for (a) $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$ and (b) $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$.

Table 3
Temperature programmed desorption of NH_3 for various catalysts.

Catalyst	T_{des}[a]/°C	Peak area[b]/a.u.	T_{des}[c]/°C	Peak area[b]/a.u.	Total peak area[b]/a.u.
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$	229	3095	470	2404	5499
$Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$	229	2421	–	–	2421

[a] Lower temperature peak for weak acid sites.
[b] The peak area was calculated by Gaussian fitting method.
[c] Higher temperature peak for strong acid sites.

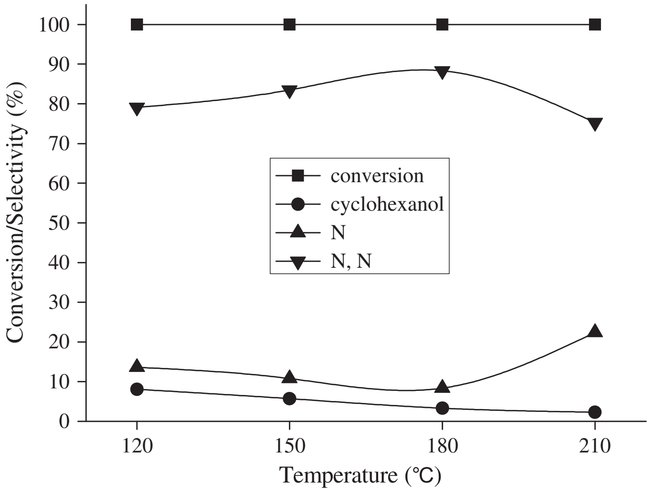


Fig. 4. Influence of the temperature on the reductive amination over $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$.Reaction conditions: hydrogen pressure = 4.0 MPa; flow rate = 0.2 mL/min; cyclohexanone: 1,6-diaminohexane (mole) = 2:1; concentration in 1,4-dioxane = 20.0 wt.%.

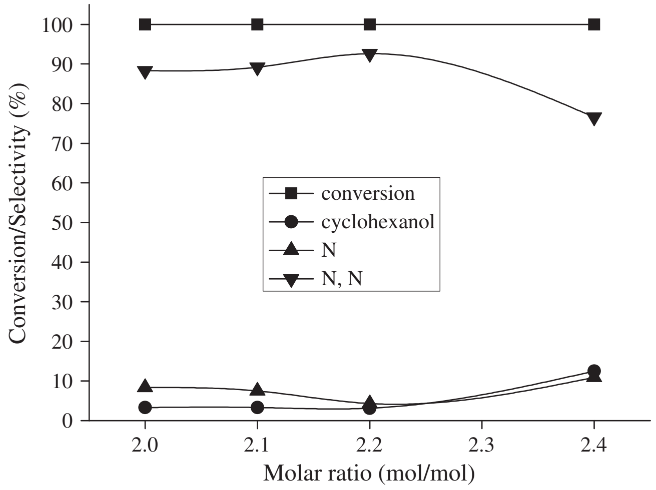


Fig. 5. Influence of molar ratio of cyclohexanone to 1,6-diaminohexane.Reaction conditions: temperature = 180 °C; hydrogen pressure = 4.0 MPa; flow rate = 0.2 mL/min; concentration in 1,4-dioxane = 20.0 wt.%.

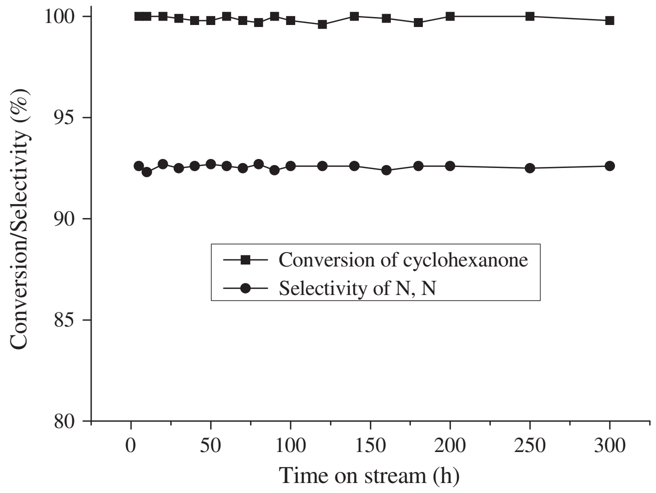


Fig. 6. Lifetime of $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$.

decreased accordingly. Thus, the molar ratio of cyclohexanone to 1,6-diaminohexane was selected as 2.2.

3.5. The stability of catalyst

Finally the stability of $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3\text{-}AB_{35}$ was tested with time-on-stream for 300 h under optimum reaction conditions and the results are shown in Fig. 6. Clearly no deactivation occurred in the reductive amination at 180 °C. The conversion of cyclohexanone and selectivity of N, N′-dicyclohexyl-1,6-diaminohexane were higher than 99% and 92% over the entire reaction time, respectively. Therefore, the catalyst is promising for pilot plant test.

4. Conclusion

Alumina B modified $Cu_{20}Cr_5La_5/\gamma\text{-}Al_2O_3$ was certified suitable for the reductive amination of cyclohexanone with 1,6-diaminohexane in a continuous process. The addition of alumina B remarkably decreased the acidity of catalyst but had no influence to the active spices. The low acidity could inhibit the dehydration of cyclohexanol and the aldol condensation of cyclohexanone, furthermore, the low acidity facilitated the desorption of amino compounds from the surface of catalyst. The hydrogenation of cyclohexanone on the surface of catalyst was irreversible at low temperature but reversible at higher temperature, and 180 °C was selected as the reaction temperature. The selectivity of N-cyclohexyl-1,6-diaminohexane was mainly affected by molar ratio of starting materials and reaction temperature. The stability of the catalyst was tested for 300 h under optimum reaction conditions, and the conversion of cyclohexanone and selectivity of N, N′-dicyclohexyl-1,6-diaminohexane were higher than 99% and 92% over the entire reaction time. This process is promising for large-scale industrial production.

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