



Research Article

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Study on Ag-based catalysts for synthesis of indole

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ABSTRACT

A series of Ag-based catalysts for the synthesis of indole by the reaction of aniline and ethylene glycol were prepared and characterized by XRD. The results indicated that the activity and stability of Ag/SiO₂ catalyst were increased after adding Zn, Mn, Cd, Mg and Ca promoters. The reason why they could increase the stability of the catalyst might be due to them possessed basic properties and excellent performance of dehydrogenation and dehydration. For the catalysts, there were two main causes of deactivation during the reaction: carbon deposition and silver sintering at 300-400°C. The activity and selectivity strongly depend on the loading amount and grain size of Ag. The catalysts with small grain size of Ag had higher activity than those with big grain size. Some catalysts showed high catalytic activity in this reaction.

Keywords: Indole, Ag-based catalysts, Promoters, Synthesis, Aniline, Ethylene glycol.

INTRODUCTION

Since the first separation of indole by Baeyer[1] in 1866, this heterocycle has attracted considerable interest understandably arising from its important substructure of numerous nature and pharmacologically active compounds[2-3] such as bufotenine or lysergide. Many approaches to the construction of the indole skeleton had been reported [4-11]. From an industrial point of view, one of the most promising routes for synthesis of indole might be condensation of aniline with ethylene glycol due to short procedure and inexpensive materials. In the reaction, transition metal-catalyzed heteroannulation processes had been widely introduced. Honda Tadaoshi[12] prepared Ag-ZnO-Co catalyst and Mitsui Toatsu Chemicals[13] reported CdS as catalyst. However, these catalysts were expensive or poisonous. A catalyst with easy preparation, less cost, less toxicity and high activity for the intermolecular cyclization of aniline with ethylene glycol to indole was still in high demand.

In the paper, different Ag-based catalysts were prepared, characterized and employed for the synthesis of indole and some valuable results were obtained.

EXPERIMENTAL SECTION

preparation of catalyst by co-precipitation method

A solution of No.1 water glass (containing 25.2% of SiO₂, 7.5% of Na₂O) in water was mixed with a solution of nitrates in water. After the mixture was neutralized with an aqueous ammonia solution, the precipitate formed was thoroughly washed with water, dried at 120°C for 3 hours, calcined at 500°C for 4 hours and extruded to bars of 2-3mm diameter.

preparation of catalysts by impregnation method

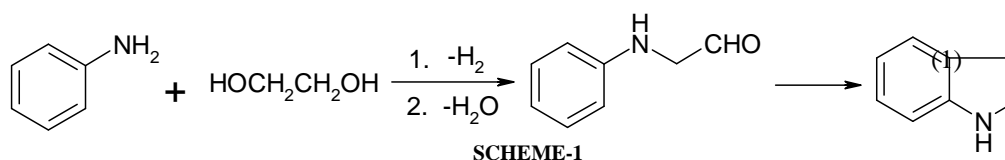
The catalysts were prepared by incipient-wetness impregnation method. After impregnating SiO₂ (macroporous silica gel, 120-240m²/g, 200-600Å) in the corresponding nitrates aqueous solution for 24h at room temperature, the sample was dried at 120°C for 3 h, then calcined at 500°C for 4 h to obtain the catalyst.

Catalyst characterization

The amounts of all components in the Ag-based catalyst were determined by inductively coupled plasma torch (ICP-AES) (Vista MPX). The specific surface areas of catalysts were measured by NOVA 2000 (Quantachrome, USA) using N₂ as adsorption at 77.40K. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2500 X-ray diffractometer with CuKα radiation, 40KV, 200mA and in the range 10-80°.

Catalytic activity test and analysis

The experiment was carried out in a fixed catalyst bed with 60ml of calcined catalyst. Before each run, the catalyst was reduced in a stream of H₂ at 300°C for 4 hours. Then the internal temperature of the reactor was kept at 340-350°C and the pressure was kept at 8.0×10⁵ Pa. A mixture consisting of 5moles of aniline and 1mole of ethylene glycol and water was introduced respectively into the evaporator at 30 ml/h and 9 ml/h. The condensate was sampled out from the gas/liquid separator once two hours and analyzed by gas chromatography using a 25 m capillary column filled with SE30. Product was identified by ¹H NMR.

**RESULTS AND DISCUSSION**

According to the reaction mechanism, a catalyst should have excellent performance of dehydrogenation and dehydration for the synthesis of indole with aniline and ethylene glycol. As is well known, silver is proved to be an effective metal in dehydrogenation. However, it is unstable as a catalyst in high temperature (>300°C). In order to improve its stability, modified Ag-based catalysts containing different additives, such as Zn, Mn, Cd, Co, Mg, Ca or their combination were developed by our work. The activity of the additives was listed in table-1.

Table-1 The activity of catalyst promoter for the synthesis of indole

Catalyst	Preparation method	Conversion of ethylene glycol (%)	Selectivity of indole(%)
Cu ₂₀ /SiO ₂	impregnation method	98.0	45.9
Mn ₂₀ /SiO ₂	impregnation method	62.7	46.5
Ce ₂₀ /SiO ₂	impregnation method	50.2	12.7
Fe ₂₀ /SiO ₂	impregnation method	65.4	43.2
Ba ₂₀ /SiO ₂	impregnation method	61.0	45.4
Zn ₂₀ /SiO ₂	impregnation method	67.6	24.9
Cd ₂₀ /SiO ₂	impregnation method	57.7	74.6
Co ₂₀ /SiO ₂	impregnation method	54.1	74.2
Cr ₂₀ /SiO ₂	impregnation method	61.6	50.5
Ni ₂₀ /SiO ₂	impregnation method	67.5	29.7
5%SmCl ₃ /SiO ₂	impregnation method	81.1	36.6

a. The number in this column denotes the weight percentage of each element in the final catalyst.

b. Reaction conditions: 340-350°C, LHSV=0.65h⁻¹, n(aniline):n(ethylene glycol)=5:1.

Based on the above results, we prepared some Ag-based catalysts, and conversion rate of ethylene glycol and selectivity of indole given in table-2.

Table 1 and table 2 indicated that Zn could efficiently improve the dispersion of silver on the support and inhibit the sintering of silver crystallite during the reaction process. Zn is a structure promoter. Zn₉/SiO₂ was prepared by a coprecipitation method, then Ag₁₀ was loaded by the incipient wetness impregnation method. The activity and selectivity strongly depend on the Ag loading. When Ag loading was too high, both the activity and selectivity decreased. Ca, Mg, and Mn were good promoters. However, Co reduced the activity of the catalyst. Some catalyst promoters had high activity used separately, but the activity of catalysts combined with other components was not high. Amount of Zn-Mg-Ca loaded in the Ag-based catalyst affected the activity of catalysts. When the Zn-Mg-Ca: SiO₂=9%, the conversion of ethylene glycol reached 98.8% and selectivity for the synthesis of indole exceeded 80.2%, which was higher than the results over the Ag₉-Zn_{2.5}-Mg_{0.5}-Ca_{0.3}/SiO₂ catalyst and Ag₉-Zn₄-Mg_{1.4}-Ca_{0.7}/SiO₂ catalyst. Fig.1 showed the XRD pattern of reduced Ag-Zn/SiO₂ sample.

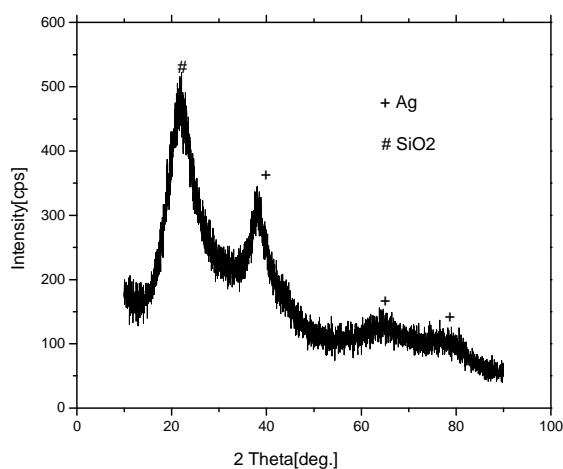
Table-2 The results of indole synthesis over Ag-based catalysts

Catalyst	Preparation method	Conversion of ethylene glycol (%)	Selectivity of indole(%)
Ag ₂₀ /SiO ₂	impregnation method	97.0	35.1
Ag ₁₀ -Zn ₇ /SiO ₂	impregnation method	96.8	79.5
Ag ₁₀ -Zn ₉ /SiO ₂	co-precipitation method +impregnation method	98.0	77.1
Ag ₆₉ -Zn ₁₅ -Mn ₃ /SiO ₂	co-precipitation method	85.4	13.6
Ag ₇ -Zn ₄ -Mn ₁ /SiO ₂	impregnation method	98.0	76.1
Ag ₁₀ -Zn ₉ -Co _{0.1} /SiO ₂	co-precipitation method +impregnation method	83.4	5.3
Ag ₉ -Zn ₆ -Ca ₂ /SiO ₂	impregnation method	97.8	76.6
Ag ₉ -Zn _{2.5} -Mg _{0.5} -Ca _{0.3} /SiO ₂	impregnation method	95.7	78.0
Ag ₉ -Zn ₃ -Mg ₁ -Ca _{0.5} /SiO ₂	impregnation method	98.8	80.2
Ag ₉ -Zn ₄ -Mg _{1.4} -Ca _{0.7} /SiO ₂	impregnation method	96.6	78.6
Ag ₉ -Cd ₅ -Mg ₂ -Ca ₁ /SiO ₂	impregnation method	98.2	83.5

a. The number in this column denotes the weight percentage of each element in the final catalyst.

b. In Ag₁₀-Zn₉/SiO₂, Ag₆₉-Zn₁₅-Mn₃/SiO₂ and Ag₁₀-Zn₉-Co_{0.1}/SiO₂, the main active ingredient Ag was loaded by impregnation method, other ingredients were loaded by co-precipitation method.

c. Reaction conditions: 340-350°C, LHSV=0.65h⁻¹, n(aniline):n(ethylene glycol)=5:1.

**Fig. 1** XRD Pattern of the Reduced Ag-Zn/SiO₂ Catalyst

It could be seen that the characteristic peaks of the catalysts only come from Ag⁰ with the grain size of 5nm and SiO₂ after reduction and Zn had a good dispersity.

Fig.2 showed the XRD patterns of the fresh and used for 24h catalysts of Ag₉-Zn₃-Mg₁-Ca_{0.5}/SiO₂ prepared by impregnation method.

The characteristic peaks of Zn, Mg and Ca were not exhibited. The grain size of Ag⁰ changed from 7.6nm to 10.0nm after used for 24h, but the catalyst was still a highly active catalyst for the direct synthesis of indole from aniline and ethylene glycol. For the catalyst, there were two main causes of deactivation during the reaction: carbon deposition and silver sintering. The reason why Mg, Zn and Ca could increase the stability of the catalyst might be due to that they possessed basic properties and could neutralized unnecessary acidic centers on the surface of SiO₂, which decreased carbon deposition.

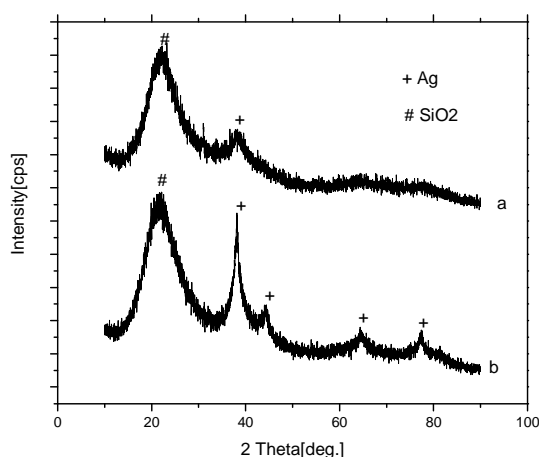


Fig.2 XRD Patterns of $\text{Ag}_9\text{-Zn}_3\text{-Mg}_1\text{-Ca}_{0.5}/\text{SiO}_2$ Catalyst
a. XRD pattern of the reduced $\text{Ag}_9\text{-Zn}_3\text{-Mg}_1\text{-Ca}_{0.5}/\text{SiO}_2$ catalyst
b. XRD pattern of the $\text{Ag}_9\text{-Zn}_3\text{-Mg}_1\text{-Ca}_{0.5}/\text{SiO}_2$ catalyst after employment for 24h

Fig.3 showed the XRD patterns of the fresh and used for 24h catalysts of $\text{Ag}_9\text{-Cd}_5\text{-Mg}_2\text{-Ca}_1/\text{SiO}_2$ prepared by impregnation method .

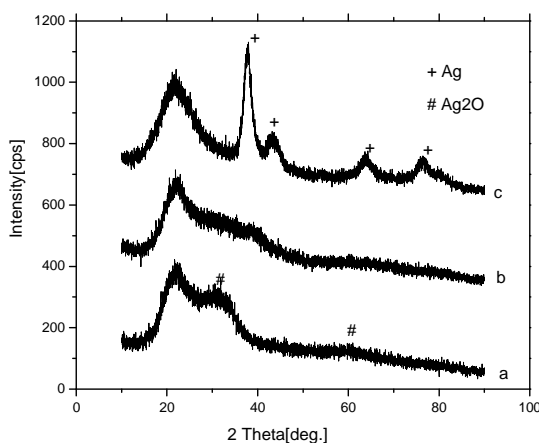


Fig.3 XRD Patterns of the $\text{Ag}_9\text{-Cd}_5\text{-Mg}_2\text{-Ca}_1/\text{SiO}_2$ Catalyst
a. XRD pattern of the calcined $\text{Ag}_9\text{-Cd}_5\text{-Mg}_2\text{-Ca}_1/\text{SiO}_2$ catalyst
b. XRD pattern of the reduced $\text{Ag}_9\text{-Cd}_5\text{-Mg}_2\text{-Ca}_1/\text{SiO}_2$ catalyst
c. XRD pattern of the $\text{Ag}_9\text{-Cd}_5\text{-Mg}_2\text{-Ca}_1/\text{SiO}_2$ catalyst after employment for 24h

The characteristic peaks of the calcined $\text{Ag}_9\text{-Cd}_5\text{-Mg}_2\text{-Ca}_1/\text{SiO}_2$ catalyst only came from Ag_2O and disappeared after reduction. It showed that Ag, Cd, Mg and Ca had better dispersity in the catalyst than Ag, Zn, Mg and Ca in the $\text{Ag}_9\text{-Zn}_3\text{-Mg}_1\text{-Ca}_{0.5}/\text{SiO}_2$ catalyst. As a result, the $\text{Ag}_9\text{-Cd}_5\text{-Mg}_2\text{-Ca}_1/\text{SiO}_2$ catalyst had higher activity than $\text{Ag}_9\text{-Zn}_3\text{-Mg}_1\text{-Ca}_{0.5}/\text{SiO}_2$ catalyst for the synthesis of indole. The emergence of characteristic peaks of Ag° indicated that Ag° was sintered with the grain size of 6.6nm after used for 24h.

CONCLUSION

The activity of the Ag-based catalysts was mainly related to the grain sizes of Ag. XRD results indicated that catalyst promoters, such as Cd, Zn, Mn, Ca and Mg, could efficiently improve the dispersion of Ag on the support and increased the activity and stability of Ag-based catalysts. The reason why Cd as promoter had higher activity than Zn might be due to them different Crystal structure and basicity.

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ICP-AES spectral analysis, NOVA 2000 analysis and XRD spectral analysis.

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