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EFFECT OF THE SUPPORT ON MANGANESE CARBON CATALYSTS FOR OXIDATION OF CYCLOHEXANONE BY MOLECULAR OXYGEN

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Introduction

- Adipic acid, which is used in the production of polyamides, polyesters, and plasticizers, is currently produced mainly by two step oxidation of cyclohexane: (1) catalytic oxidation with air to the mixture of cyclohexanol and cyclohexanone;
  (2) oxidation with nitric acid.
- The use of nitric acid in the second step leads to NOx pollution.
- Carbons are high-surface-area materials and offer a wide range of application as adsorbents for various compounds, and in catalysis, either as supports for the active phases, or as catalysts.
- The nature and concentration of surface functional groups of carbon materials may be modified by suitable thermal or chemical post-treatments [1].

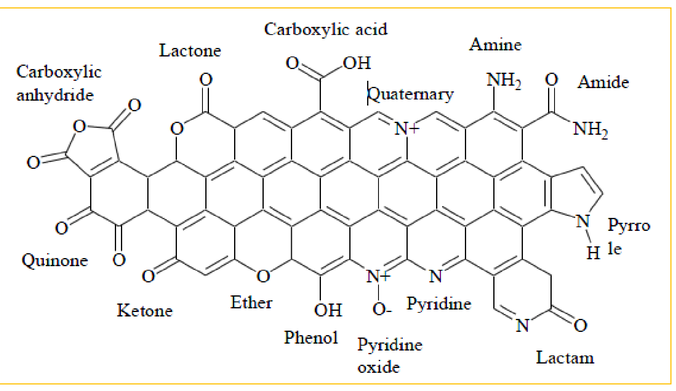
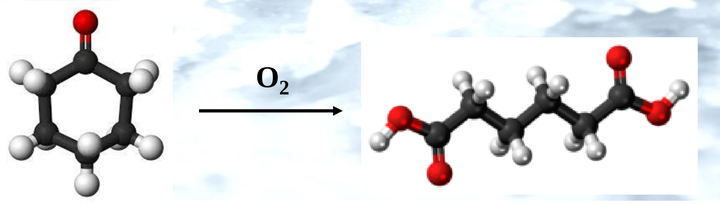


Fig.1 Surface functional carbon groups.

Aim

- In our work, the catalytic performance of Mn-based carbon catalysts in the liquid phase oxidation of cyclohexanone with molecular oxygen in the solvent-free system was studied.



Experimental

Catalysts

Commercial carbon
activated charcoal Norit (Fluka) (AC)
carbon Vulcan (carbon black XC72) (C)

drying at 105 °C for 12 h

demineralization with HCl → C-d

treatment in N_2 flow at 500 °C (700 °C or 900 °C)

AC-500 (700, 900) → C-d500

wet impregnation and calcination at 500 °C [2]

1%Mn/AC-900 → 1%Mn/C-d

Catalytic tests

Cyclohexanone: 3 ml
Catalyst: 150 mg

Oxygen pressure: 0.35 MPa

Reaction temperature: 80 – 120 °C

Fig.2 Reactor: glass-lined stainless steel with monitoring of the oxygen consumption

Method of analysis: gas chromatography
Esters of dicarboxylic acids: esterification with methanol in the presence of concentrated H_2SO_4

Results and Discussion

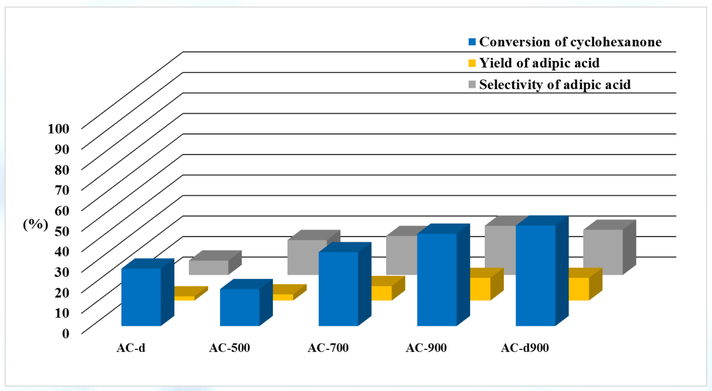


Fig.3 Oxidation of cyclohexanone over activated charcoal Norit based catalysts in experiments carried out at 90 ℃ and 0.35 MPa O_2, 210 min.

Table 1
Oxidation of cyclohexanone over activated charcoal Norit catalysts

Catalyst	Conversion (%)	Yield of acid (mol %)			
		Adipic	Glutaric	Succinic	Oxalic
AC-d	28	2	0	0	0
AC-500	18	3	1	1	0
AC-700	36	7	2	2	0
AC-900	45	11	2	1	0
AC-d900	49	11	2	2	0

Reaction conditions: 90 ℃, 0.35 MPa, O_2, 150 mg of catalyst, 210 min

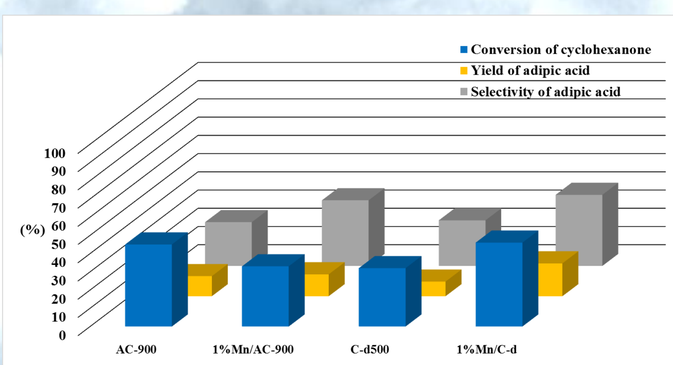


Fig.4 Oxidation of cyclohexanone over activated charcoal Norit and carbon black Vulcan supported manganese catalysts.

Table 2
Oxidation of cyclohexanone over activated charcoal Norit and carbon black Vulcan supported manganese catalysts

Catalyst	Conversion (%)	Yield of acid (mol %)			
		Adipic	Glutaric	Succinic	Oxalic
AC-900	45	11	2	1	0
1%Mn/AC-900	33	12	2	2	0
C-d500	32	8	2	2	0
1%Mn/C-d[a]	46	18	5	3	0

Reaction conditions: 90 ℃, 0.35 MPa, O_2, 150 mg of catalyst, 210 min, [a]110 min

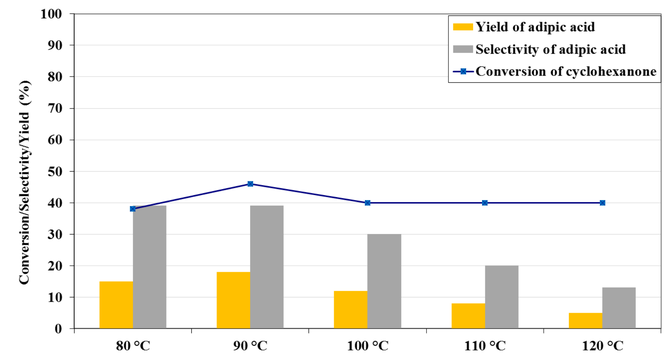


Fig.5 Oxidation of cyclohexanone over the 1%Mn/C-d catalyst in experiments carried out at 80 ℃ 175 min, at 90 ℃ and 100 ℃ 110 min, at 110 ℃ and 120 ℃ 40 min, and 0.35 MPa O_2.

Conclusions

- The treatment of activated charcoal Norit at different temperatures strongly influences the conversion of cyclohexanone and selectivity to diacids.
- In accordance with literature findings [3], the thermal treatment of active carbon reduces the amount of acidic groups present on its surface and create basic groups such as pyrone type.
- Addition of manganese to activated charcoal Norit treated in nitrogen at 900 °C caused a decrease in the catalytic activity and had only minor effect on the adipic acid formation compared to the pure Norit catalysts.
- On the other hand, adding Mn to demineralized carbon black Vulcan greatly enhanced the reaction rate and formation of adipic acid.
- A signifficant influence of reaction temperature on the oxidation of cyclohexanone over Mn based carbon black Vulcan catalyst was observed.

References

[1] Figueiredo J. L., Pereira M. F. R., Freitas M. M. A., Órfao J. J. M., Carbon *37*, 1379 (1999).
[2] Zou G., Zhong W., Xu Q., Xiao J., Liu C., Li Y., Mao L., Kirk S., Yin D., Catal. Commun. 58, 46 (2015).
[3] Besson M., Gallezot P., Perrard A., Pinel C., Catal. Today 102-103, 160 (2005).

Acknowledgement

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