

A STUDY ON THE OXIDATIVE CARBONYLATION OF ANILINE

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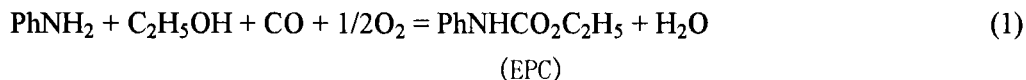
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Abstract The oxidative carbonylation of aniline to carbamate over Pd-based catalyst was studied by using NaI and absolute ethanol as the promoter and solvent, respectively. The optimum process conditions for this reaction were investigated. At 170 °C, after 2 h of reaction, the Pd/C catalyst exhibited high activity (97.49%) and high selectivity (85.26%). The promoter role of NaI was discussed, and a mechanism for the title reaction was proposed.

Keywords aniline, carbamate, oxidative carbonylation, Pd-based catalyst

Introduction

The product of aniline oxidative carbonylation is diphenylurea or carbamate, both of them can easily turn into isocyanate, which is widely used to make artificial leather, adhesive agent, elastic body, fabric and synthesis rubber. It is an important raw material for polyester industry^[1]. The stoichiometric equation is shown as below:



There are some people studying this reaction, but they focused their attention on the selection of catalyst and reaction conditions^[2-4]. A few paper reported the mechanism of

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this reaction^[1,5,6], but these mechanisms were very different in many aspects, especially, the role of promoter NaI in this reaction has not been known so far. Most people used Pd as the catalyst for this reaction, but none of them have compared the activity of various Pd-based catalysts. In the present work, we found that all the Pd-based catalysts have the same catalytic activity; moreover, the result of XPS showed that the active components on these catalysts may turn into a same species after reaction, which give us some clues for the mechanism of aniline oxidative carbonylation. We also explained the promoter role of NaI on the basis of experimental results.

Experimental

Into a 100 mL autoclave equipped with an electric stirrer and an automatic temperature controller were charged 50 mg of Pd/C (3 wt% of Pd on activated carbon), 20 mg sodium iodide, 40 mL absolute ethanol, 2.30 g aniline and 1.000 g diphenyl as internal standard. After the air inside the autoclave was replaced with CO, CO was pressurized into the autoclave to 6.0 MPa and then oxygen was pressurized, resulting in a total pressure of 6.7 MPa. The reaction was carried out at 170°C~180°C for 2 h with stirring, subsequently, the reaction mixture was cooled to room temperature, and then analyzed by GC.

Results and discussion

Catalytic performance of Pd/C catalyst

1. Reuse information of catalyst

We found that the Pd/C catalyst can still remain its catalytic activity after being used ten times.

Table 1 Reuse information of catalyst

Expt. times	1	2	3	4	5	6	7	8	9	10
Conversion of aniline / %	88.5	95.0	87.6	91.5	95.2	96.0	96.5	89.8	96.7	92.1
Selectivity to carbamate / %	90.8	91.6	91.5	87.7	87.8	87.7	97.2	80.5	79.6	80.4

2. Effect of temperature on catalytic activity

Temperature has a great effect on aniline oxidative carbonylation. We have studied the activity of catalyst at various temperatures. The results are listed in Table 2.

Table 2 Effect of temperature on the activity of 5% Pd/C catalyst

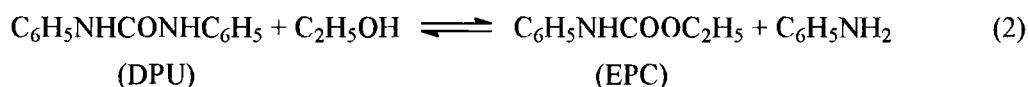
Temperature/°C	100	140	150	160	170	177	185	200
$C_{AN}/\%$	62.13	84.71	95.25	98.71	97.49	99.41	93.16	97.75
$S_{EPC}/\%$	0	70.40	79.87	79.85	85.26	82.91	81.09	73.43
Yield / %	0	59.63	76.08	78.82	83.12	82.42	75.54	71.78

$C_{AN}/\%$: conversion of aniline ; $S_{EPC}/\%$: selectivity to EPC

Reaction condition: reactive time, 2 h; dose of NaI, 40 mg; absolute ethanol, 40 mL;

$P_{CO}=6.0$ MPa; $P_{O_2}=0.7$ MPa

The results show that 170°C~180°C are the optimum temperatures for this reaction. When the reaction temperature is lower than 100°C, the main product is diphenyl urea (DPU); and high above 150°C, ethyl phenylcarbamate (EPC) is the main product. When the temperature is between 100°C~150°C, EPC and DPU could be both detected, and there is a conversion equilibrium between EPC and DPU.



This equilibrium tends to move to the left side, but when the temperature is high to 170°C and the solvent ethanol is excessive, EPC can become the main product.

Results of using other Pd-based catalyst

1. Activity of various Pd-based catalysts

It is well known that in the reductive carbonylation of aromatic nitro compound, only $PdCl_2$ has catalytic activity and other Pd-based catalysts like Pd^0 or PdO has no activity^[7-8]. But in aniline oxidative carbonylation^[7-8], we found that almost all the Pd-based catalysts had the same activity (see Table 3).

Table 3 Activities of various Pd-based catalysts

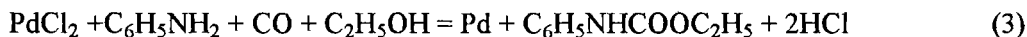
Catalyst	Catalyst dose / mg	$C_{AN}/\%$	$S_{EPC}/\%$
$PdCl_2$	2.9	97.59	82.31
PdO	48.2	99.45	87.31
0.75% $PdCl_2$ /Silicon	245.1	95.31	81.69
3%Pd/C	53.1	97.49	85.10

Reaction condition: temperature, 177°C~180°C; $P_{CO}=6.0$ MPa; $P_{O_2}=0.7$ MPa

reaction time, 2 h~2.5 h; NaI=35 mg; aniline=2.3 g

This result implies that the activity of Pd-based catalysts does not rely on its initiative configuration. We can infer that the active components on these Pd-based catalysts may transform into an identical species in the reaction and then enter the catalytic cycle.

We regard that this identical species is a mixture of Pd and PdO. If PdCl₂ is the catalyst used, it will oxidize aniline at first and will be reduced to Pd⁰, then Pd⁰ is oxidized to PdO by oxygen. In fact, at the early stage, it was PdCl₂ but not oxygen that oxidized aniline to carbamate^[9,10]. The reaction equation is shown as below:



This reaction equation shows that even though the Pd²⁺ is used, it will soon become Pd⁰. Due to the existence of oxygen, Pd⁰ will transform into PdO inevitably, then go into the catalytic cycle. But oxygen in this reaction will be used up (though oxygen is excessive, ethanol and carbon monoxide are both excessive too, they can consume oxygen), so it is certain that some of Pd⁰ will turn into PdO and the other will not. Therefore, the catalyst obtained after reaction always contains Pd⁰ and PdO (see 3).

2. Promoter role of iodide

Iodide as promoter is necessary for aniline oxidative carbonylation, but catalytic dosage of iodide is enough. We also found that PdI₂ had the identical catalytic activity as Pd+NaI, which implies that iodide might play its role by affecting catalyst but not reagents or products. So far no other substances have been found which can replace iodide to promote oxidative carbonylation of aniline. The promoter role of iodide in this reaction is still unknown, even though there is few publication involving this problem. We found that when iodide is absent, the oxidation of aniline can occur but the carbonylation can not, thus the coordination of I⁻ may increase the electron density of Pd and let CO gain more feedback electrons. Pd²⁺ is a kind of soft acid and I⁻ is soft base, so I⁻ can be easily coordinated to Pd²⁺; at the same time, not only I⁻ has plenty of 5*p* electrons which are well matched with 4*d* electrons of Pd²⁺ in energy, but also it is not π-acid, so it will not share electrons feedback from Pd with CO.

3. Results of XPS

The XPS experiments of three kinds of catalysts were carried out. The results show that no matter what Pd-based catalysts are used, they all have the same binding energy after reaction; so the active components on these catalysts might have turned into the same species, which might be a mixture of Pd and PdO.

Table 4 Results of XPS

Catalyst	Binding energy of $3d_{3/2}$ / eV*	
	Before reaction*	After reaction
PdO	336.8	335.3
3%Pd/C	334.6	335.0
0.75%PdCl ₂ /Silicon	336.2	335.2

*: C 1s (284.7 eV) was used as the standard of binding energy.

At last, we propose the mechanism of aniline oxidative carbonylation as follows:

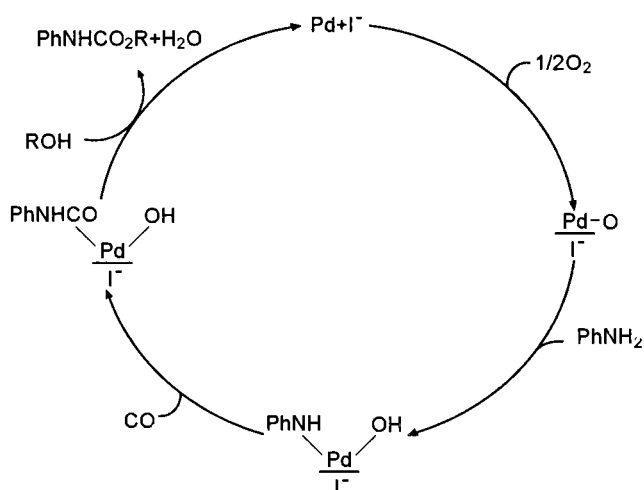


Fig.1 Proposed mechanism of aniline oxidative carbonylation

Conclusions

1. Pd/C catalyst exhibits high activity (97.49%) and high selectivity (85.26%) in aniline oxidative carbonylation. This catalyst also has high stability, it can remain its catalytic activity after being used ten times.

2. The proper reaction temperature is between 170°C~180°C. Only at or above this temperature, the equilibrium between byproduct (DPU) and main product (EPC) can move to EPC. However, if the temperature is too high (>180°C), deep oxidation may occur.

3. All the Pd-based catalysts have the same catalytic activity, which implies that these catalysts may transform into an identical species in reaction and then enter the catalytic cycle.

4. Aniline oxidative carbonylation can not proceed without I⁻, moreover, no other

promoter can replace I⁻ to promote this reaction. We propose that the coordination of I⁻ to Pd²⁺ increases the electron density of Pd²⁺, enables Pd²⁺ to have enough electron to feedback to CO, which makes carbonylation proceed easily.

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杂多化合物催化异丁烯氧化反应 (Oxidation of Isobutene Catalyzed by Heteropoly Compounds) / 何达云, 吴京琳, 钟邦克 (暨南大学化学系 广东 广州 510632) // *J.Nat.Gas Chem.*, 2000, 9: 217

摘要 用流动反应器、XRD、IR和DTA等方法对杂多化合物的组成和结构以及在异丁烯部分氧化中的催化行为进行了研究, 发现在 $\text{PMo}_{12}\text{As}_6\text{Cu}_{0.1}\text{O}_x$ 中加进适量的K和V得到的杂多化合物在异丁烯一步氧化为甲基丙烯酸的过程中显示出良好的催化性能。通过调变化化剂的组成和优化反应条件, 甲基丙烯酸和甲基丙烯醛总收率达67%。V和K加入到母体磷钼酸(PMo_{12})中增强了热稳定性, 和母体相比催化剂的分解温度提高了200°C。**关键词** 杂多化合物 氧化 异丁烯 甲基丙烯酸 甲基丙烯醛

无机膜反应器用于正丁烷氧化制顺丁烯二酐的研究 (Oxidation of *n*-Butane to Maleic Anhydride over an Inorganic Membrane Reactor) / 黄仲涛, 纪红兵, 姜红霞, 王乐夫 (华南理工大学化工学院 广东 广州 510641) // *J.Nat.Gas Chem.*, 2000, 9: 223

摘要 通过浸渍法在中孔 $\gamma\text{-Al}_2\text{O}_3$ 膜上制备出V-P-Co-Ce-O多组分金属氧化物催化膜, 将之应用于非燃料电池型催化膜反应器并研究其可行性及正丁烷制顺丁烯二酐的反应特性。考察了反应温度、空速和吹扫气流速对催化活性的影响, 对膜反应器的稳定性也进行了简单的测试。实验证明, 与固定床相比, 膜反应器具有更高的反应转化率和选择性。

关键词 V-P-Co-Ce-O多组分金属氧化物催化膜 正丁烷 顺丁烯二酐

不同制备方法对Ba/MgO催化剂催化甲烷氧化偶联反应性能的影响 (Effects of Preparation Methods on the Catalytic Properties of Ba/MgO Catalysts in Oxidative Coupling of Methane) / 达建文 (齐鲁石化公司研究院 山东 淄博 255400) 沈师礼 (石油大学(北京)化学学部 北京 102200) // *J.Nat.Gas Chem.*, 2000, 9: 231

摘要 采用BET、XRD、SEM和XPS等方法对Ba/MgO催化剂进行了分析, 并且对该催化剂对甲烷氧化偶联反应的性能进行了测试。结果表明, 制备方法对Ba/MgO催化剂的催化性能有很大影响。采用淤浆法制备的Ba/MgO催化剂具有合适的比表面积和表面物种分布, 因此对甲烷转化显示出良好的催化活性。而采用机械混合或浸渍等方法制备的催化剂由于表面不均匀以及表面烧结等原因其活性较差。

关键词 Ba/MgO 制备方法 催化性能

中孔硅酸盐材料MCM-41的合成与表征研究 (Synthesis and Characterization of Mesoporous Aluminosilicate MCM-41) / 宋春敏, 阎子峰 王怀平 (石油大学重质油加工国家重点实验室 山东 东营 257062) Lu Max (The University of Queensland, Australia) // *J.Nat.Gas Chem.*, 2000, 9: 237

摘要 以十六烷基三甲溴化铵为模板剂, 硅酸钠为硅源, 铝酸钠为铝源, 在水热条件下成功地合成了MCM-41中孔硅酸盐材料。采用XRD、低温 N_2 吸附脱附等测试手段对合成的MCM-41样品进行了表征。通过优化合成条件, 合成出孔径3.2 nm、比表面 $904\text{ m}^2/\text{g}$ 和孔壁厚约1.46 nm的MCM-41分子筛。催化活性测定采用微反应活性实验来评价其活性和选择性。

关键词 分子筛 合成 表征 MCM-41

苯胺氧化羰基化研究 (A Study on the Oxidative Carbonylation of Aniline) / 王文峰¹, 张藩贤², 许翩翩² (福州大学化学系 福建 福州 350002; ²厦门大学化学系 福建 厦门 361005) // *J.Nat.Gas Chem.*, 2000, 9: 243

摘要 以Pd/C为催化剂, 以NaI为助催化剂, 以无水乙醇为溶剂, 进行了苯胺氧化羰基化反应。研究了苯胺氧化羰基化的最佳工艺条件, 解释了碘化钠在本反应中所起的助催化作用。在170°C, 反应两小时后, Pd/C显示了高活性(97.49%)和高选择性(85.26%)。最后, 提出了苯胺氧化羰基化反应的机理。

关键词 苯胺 氨基甲酸酯 羰基化 机理

费托(FT)合成及相关反应的研究进展 (New Developments in Research Based on FT Synthesis) / 王德生, 关乃佳 (南开大学化学系新催化材料研究室 天津 300071) // *J.Nat.Gas Chem.*, 2000, 9: 249

摘要 按催化剂分类介绍了改性FT合成及与其相关反应的近期研究成果。即通过调制催化剂组成和反应条件, 由合成气直接合成其他有价值的化工原料如醇、烯烃、芳香烃和石蜡等。分子筛, 如Al-MCM-41和ZSM-5/磷铝分子筛等在FT及其相关反应中扮演着越来越重要的角色, 但由于金属作为反应活性中心, 所以金属催化剂如Fe、Co、Pd、Rh和Ni, 双金属如Fe-Ir和Pt-Mo仍然是人们研究的重点。另外, 一些新的反应方法和新的材料也被采用, 如超临界方法及超微粒催化剂等。

关键词 改性FT合成 金属催化剂 分子筛