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Selective Oxidation of Benzene to Phenol

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Incentives

An opportunity for a new market for BU catalysts, \$20 million/year for 2001 and beyond. Catalyst will directly oxidize benzene to phenol to replace the current 4.5 billion pounds phenol, three-step cumene process. Proposed catalyst will eliminate acetone as a byproduct in an over-supplied market. Catalyst will save energy by 65 trillion Btu/year by 2020, and minimize waste by 50 billion tons/year. Project was ranked high priority by chemical experts.

Objectives

Develop a catalyst for the selective direct oxidation of benzene to phenol in one step. The single pass yield should be at least 50%, with a few or no organic by-products.

Progress Report 1998-1999

The object of the project was to selectively oxidize benzene to phenol using a conventional oxidant. The project was initiated in Collaboration with Argonne National Labs (ANL) (Chris Marshall/Lennox Iton), and Northwestern University (NWU) (Harold Kung).

Akzo Nobel tested O_2 and NO_2/O_2 as oxidants. ANL investigated the oxidation of benzene using nitric acid as it was shown to give good yield to phenol in several reports in literature. NWU worked on an alternative route to synthesize phenol starting from toluene.

Akzo Nobel

At Akzo-Nobel, Dobbs Ferry, preliminary runs conducted by F. Sherif using copper-based catalysts and a mixture of NO_2+O_2 as oxidant showed up to 20% yield to phenol. However NO_2 was abandoned due to safety constraints, as well as toxicity related issues.

A series of catalysts synthesized by F. Sherif was tested for vapor-phase oxidation of benzene with O_2 . None of these catalysts showed any selectivity to phenol. In most cases, the only products were those of combustion.

Experiments using nitric acid as oxidant were also tried at AN-DF, but no phenol was detected. This was probably due to the mild conditions. It was decided to conduct the same reaction in an autoclave under elevated temperature and pressure. Meanwhile, the team at ANL was not able to reproduce previous reports of phenol formation from benzene using nitric acid as an oxidant.

An economic evaluation was conducted at AN-DF on the use of nitric acid as a stoichiometric oxidant; it was concluded to be uneconomical. An alternative approach was to adopt a two-step process, i.e. one-pass conversion using HNO_3

followed by oxidation of by-product NO_2 to regenerate HNO_3 using O_2 from the air. The two-step process, however, is similar to the previously practiced Raschig process, which used HCl , and an oxychlorination process, where HCl was recycled. The Raschig process has been replaced by the Cumene process because of environmental and economic reasons. Therefore, it does not appear that using a process where NO_2 is recycled will be economical. The only economical route using HNO_3 would be one where HNO_3 is a catalyst for the reaction, and can be used in trace amounts so that its disposal can be accomplished without much expense. This approach remains to be tested.

Argonne National Laboratory

The project was officially begun in January, 1999 and terminated in August, 1999. Argonne team members: Christopher L. Marshall, Elizabeth A. Gardner and Lennox E. Iton

In the 6 months work with Akzo Nobel Corporation, the following was accomplished. A post doctoral appointee (Elizabeth Gardner/Michigan State University) was hired to work on the catalyst synthesis and testing phase. She completed an exhaustive literature search on single step oxidation of benzene and toluene to phenol.

In conjunction with Akzo and Northwestern University a work plan that was established. This plan divided the work along feed lines with Argonne working on a benzene feed catalyst and Northwestern working on catalysts to convert toluene to phenol.

At Argonne, in the first 4 months we designed and constructed fixed bed catalyst testing unit at Argonne National Laboratory. This required the purchasing of necessary equipment, completion of a unit safety review, and verification and commissioning of the unit.

Several catalysts were synthesized for testing in this fixed bed unit. These included Fe-ZSM-5, Tungsten polyoxometalate (W-POM), Fe on silica, and Mo on silica. All catalysts were tested using nitrobenzene as the oxidant based on the work of J. Yoo (Amoco retired). All catalysts were shown to have high activity and selectivity for nitrobenzene but low selectivity for phenol. Further discussions with Yoo resulted in suggestions regarding catalyst synthesis and pre-treatment. None of these suggestions resulted in improved phenol yield.

As a final task in this program, we conducted literature search on combinatorial testing of heterogeneous catalysts. This work was begun since the number of catalyst possibilities were beyond the scope of the single plug flow unit. Using combinatorial techniques, it is believed that we can examine many more possibilities in a shorter period of time. Under this final task, a combinatorial unit for this project was designed and built under the new partnership.

Northwestern University

Work conducted at Northwestern University during this year aimed to reproduce and then extend the data reported in a patent filed by NKK Corporation of Japan¹. The patent consisted of a two step gas phase catalytic process for the oxidation of toluene to phenol using molecular oxygen. The first step employed a V_2O_5/TiO_2 catalyst, with a series of additives, for the oxidation of toluene to benzoic acid. A separate second step converted benzoic acid to phenol using a $NiO-Fe_2O_3$ bulk oxide catalyst impregnated with small amounts of sodium and vanadium.

Reactor System Construction:

A substantial amount of time was spent constructing and trouble-shooting a reaction system for the oxidation of benzaldehyde and benzoic acid where very good material balance and complete product analysis could be obtained. After about five months, a system that allowed for the selection of a toluene, benzaldehyde, or benzoic acid feed was assembled and tested. The liquid reactants are introduced by vaporization in a saturator. In the case of benzoic acid, the saturator is heated to melt the reactant. The product stream is analyzed using an HP 5890 Gas Chromatograph.

Catalyst Synthesis:

A series of catalysts was synthesized. Samples of the $NiO-Fe_2O_3$ catalyst with compositions similar to those in the patent were made. Other catalysts are an extension of the literature regarding the second step of the patented process². Literature data indicate a greater activity of catalysts promoted with 4 wt% V_2O_5 . Accordingly, a series of Ni-V-O and Mg-V-O samples were synthesized to elucidate the catalytic function of each component. Precipitation, impregnation, and suspension methods of synthesis were used to obtain samples with varying degrees of surface area. All catalysts were calcined in stagnant air at 550°C or higher. The bulk structure of each sample, characterized by x-ray diffraction, consisted of a variety of phases (See Tables I and II). Miki, et al. found that impregnation of the samples with sodium allowed high conversion and selectivity to be achieved at a higher space velocity. Therefore, sodium promoted samples were also studied.

Catalytic Activity Tests:

The activity data obtained correspond to reaction at 400°C and a space velocity of 2200-2300 h^{-1} . The feed consisted of benzoic acid, oxygen, water and helium in a molar ratio of 1/2.7/22/72, respectively. The feed flowed through a downflow reactor containing 0.5 g of catalyst diluted with 2 g of SiC to avoid adverse thermal effects. Prior to the reaction, the catalyst was treated in situ at 450°C for

30 minutes in a stream of 10% oxygen in helium. The reactor effluent was trapped at 0°C for 6 h and then dissolved in ethanol for analysis.

Reaction tests of these compounds gave mixed results as seen in Table III. The magnesium metavanadate (I) and nickel orthovanadate (II) samples were active combustion catalysts. While the magnesium orthovanadate (III) sample was not as active, it was the most selective. The phenol yields for the two magnesium vanadates were essentially the same.

Attempts to reproduce the patent results quantitatively were not successful. Table IV shows activity test results of the nickel-iron samples prepared. As indicated in the literature, the activity of the catalyst is greatly affected by the preparation details. All catalysts were coprecipitated from a nitrate solution with sodium hydroxide, dried, and then calcined in stagnant air at 800°C for 3 h. The samples differed in the amount of NaOH used in the precipitation and in the details of the calcination steps. The X-ray diffraction patterns of the catalysts indicated the presence of NiO and NiFe₂O₄. This was consistent with the phases identified in the literature. BET measurements indicated very low surface area (< 1 m²/g). The effect of sodium appears to be consistent with the literature finding. There was also a small amount of biphenyl and hydrogen produced over this catalyst.

Miki also found that addition of vanadium to the catalysts prevented deactivation and slightly increased phenol selectivity. Due to the time averaged nature of our data, deactivation effects are not readily apparent. Lines X and XI of Table V show the activities of the same catalyst on consecutive days. There appears to be no dramatic change in the catalyst from day to day, although carbon balance problems still exist.

References:

1. Shikada, T.; Miki, A.; Asanuma, M.; Watanabe, A.; Konishi, T.; Tachibana, Y.; Japan Patent, Kokoku Tokkyo Koho, JP 07017886 A2 (1995).
2. Miki, J.; Asanuma, M.; Tachibana, Y.; Shikada, T.; *Appl. Catal. A: Gen.* **143** (1996) 215-222.

Table I: Ni-V-O catalysts

XRD analysis	Preparation Method (precursors)
Ni ₃ (VO ₄) ₂ ; NiO; ^a Ni ₂ V ₂ O ₇	Precipitation of Ni(OH) ₂ -NiCO ₃ -xH ₂ O with (NH ₄) ₂ CO ₃ ; interaction w/ VOC ₂ O ₄ solution
Ni ₃ (VO ₄) ₂ ; ^a NiO; ^a Ni ₂ V ₂ O ₇	
Ni ₃ (VO ₄) ₂	
Ni ₃ (VO ₄) ₂ ; NiO	Precipitation of Ni(OH) ₂ -NiCO ₃ -xH ₂ O with Na ₂ CO ₃ ; followed by decomposition to NiO; impregnation of NiO with NH ₄ VO ₃

^a Small amount of indicated phase

Table II: Mg-V-O catalysts

XRD analysis (primary phase listed)	Precursors (in solution)
Mg ₂ V ₂ O ₇ ; Mg(VO ₃) ₂ ; ^b Mg(VO ₄) ₂ ;	NH ₄ VO ₃ ; H ₂ C ₂ O ₄ ; Mg(NO ₃) ₂
Mg ₂ V ₂ O ₇ ; Mg(VO ₃) ₂ ; ^b MgO	
Mg(VO ₄) ₂ ; Mg ₂ V ₂ O ₇ ; Mg(VO ₃) ₂	
Mg(VO ₃) ₂ ; V ₂ O ₅	NH ₄ VO ₃ ; H ₂ C ₂ O ₄ ; Mg(OH) ₂ -MgCO ₃ -
Mg(VO ₄) ₂ ; Mg ₂ V ₂ O ₇ ; Mg(VO ₃) ₂	VOC ₂ O ₄ ; Mg(OH) ₂ -MgCO ₃ -xH ₂ O

^b Small amount of indicated phase

Table III. Activity of metal vanadate catalysts for benzoic acid oxidation

Catalyst		¹ Conversion (%)	² Selectivity (%)			³ Phenol Yield	Carbon Balance
			Phenol	COx	Benzen e		
I	MgV ₂ O ₆ , Mg ₂ V ₂ O ₇ , *MgO	67.53	2.00	97.16	0.84	0.059	59.79
II	Ni ₃ V ₂ O ₈ , *NiO, *Ni ₂ V ₂ O ₇	93.61	0.06	99.54	0.40	0.004	55.10
III	Mg ₃ V ₂ O ₈ , Mg ₂ V ₂ O ₇	39.94	37.06	62.94	-----	0.055	61.16

¹ External Conversion

² Based on products observed

³ mmol phenol per g catalyst per day (6 h)

* Small amount of indicated phase

Table IV. Activity of nickel-iron catalysts

Catalyst	¹ NaOH conc	² When ground	Conversion (%)	³ Selectivity (%)			Phenol Yield	Carbon Balance
				Phenol	COx	Benzen e		
IV	2.5 M	A	22.21	30.95	69.05	-----	0.086	79.73
V	1 M	A	48.43	47.52	52.48	-----	0.424	58.30
VI	1 M	A	25.91	19.16	80.84	trace	0.007	74.37
VII	1 M	B	8.26	46.04	53.96	-----	0.062	92.75
VIII	1 M	B	21.52	18.77	81.23	trace	0.003	78.62

¹ Used for precipitation² Sample ground before (B) or after (A) calcination³ Based on products observed**Table V. Activity of impregnated Nickel iron catalysts**

Catalyst		Conversion (%)	¹ Selectivity (%)			Phenol yield	Carbon Balance
			Phenol	COx	Benzen e		
IX	0.4% Na ₂ O/NiO-Fe ₂ O ₃	51.60	33.53	66.32	trace	0.615	62.31
X	2% V ₂ O ₅ /NiO-Fe ₂ O ₃	49.76	32.84	66.21	0.95	0.257	60.92
XI	2% V ₂ O ₅ /NiO-Fe ₂ O ₃	44.67	49.50	49.39	1.11	0.291	62.58

¹ Based on products observed