

Letter

A comparative study on aniline alkylation activity using methanol and dimethyl carbonate as the alkylating agents over Zn–Co–Fe ternary spinel systems

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Abstract

The catalyst compositions of the $Zn_{1-x}Co_xFe_2O_4$ ($x = 0, 0.2, 0.5, 0.8$ and 1.0) spinel series possessing 'x' values, $x \leq 0.5$, are unique for selective *N*-monomethylation of aniline using methanol as the alkylating agent. Since dimethyl carbonate (DMC) is another potential non-toxic alkylating agent, alkylation of aniline was investigated over various Zn–Co ferrites using DMC as the alkylating agent. The merits and demerits of the two alkylating agents are compared. Catalytic activity followed a similar trend with respect to the composition of the ferrosinels systems. DMC is active at comparatively low temperature, where methanol shows only mild activity. However, on the selectivity basis, DMC as an alkylating agent could not compete with methanol, since the former gave appreciable amounts of *N,N*-dimethylaniline (NNDMA) even at low temperature where methanol gave nearly 99% *N*-methylaniline (NMA) selectivity. As in the case of methanol, DMC also did not give any *C*-alkylated products. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The increasing demands of environmental legislation have been prompting the chemical industry to minimize, or preferably eliminate, waste production in chemical manufacture. The global demand of solid acid and solid base catalysts has increased considerably in recent years since such systems often give value-added products with improved yield without creating major burdens on the environment. Alkylanilines

such as *N*-methylaniline (NMA), *N,N*-dimethylaniline (NNDMA) and toluidines are important industrial chemicals that are used extensively as starting materials for the production of dyes, pharmaceuticals and explosives [1–3]. Owing to the numerous uses of these compounds, the demand for selective and active catalysts for the reaction has grown [4–10]. However, selective synthesis of NMA is difficult; many reported systems perform both mono- and di-methylation of aniline, leading to poor selectivity for NMA. Several reports have appeared on the alkylation of aniline using methanol as methylating agent. Our recent investigations on the alkylation of aniline using differ-

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ent ferrite systems revealed that $Zn_{1-x}Co_xFe_2O_4$ and $Zn_{1-x}Ni_xFe_2O_4$ ($x=0, 0.2, 0.5, 0.8$ and 1.0) systems possessing low 'x' values are exceptionally active and selective for *N*-monomethylation of aniline, when methanol is used as the alkylating agent [11,12]. In these communications, we have highlighted some distinct features of the systems, such as their high activity at comparatively low reaction temperatures and low methanol to aniline molar ratios, prolonged stability and NMA selectivity up to 98–99% under optimized reaction conditions. Recently, it was shown that dimethyl carbonate (DMC) is very selective for the alkylation of aniline to NMA [13–16]. As an alkylating agent, methanol is much cheaper than DMC, but the alkylation using DMC is usually feasible at a comparatively lower reaction temperature than with methanol. Trotta et al. [15] reported that the reaction of aniline with DMC gave 60.5% of NMA at 91.4% aniline conversion using α -alumina coated with potassium carbonate and polyethylene glycol as the catalyst. Similar experiments using Zn–Co ferrites as catalysts revealed that they are potential systems for alkylating aniline with DMC. In the present communication, we present the results obtained with various Zn–Co ferrite systems in the alkylation of aniline using DMC and compare the influence on selectivity and conversion of the alkylating agent (methanol or DMC) with the influences of the ferros spinel structure.

2. Experimental

2.1. Catalyst synthesis and characterization

The ferros spinel systems having the general formula $Zn_{1-x}Co_xFe_2O_4$ ($x=0, 0.2, 0.5, 0.8$ and 1.0) were prepared by a low temperature, controlled coprecipitation method [17] using aqueous solutions of ferric nitrate (2.6 M), zinc nitrate (3.4 M), cobalt nitrate (3.4 M) and sodium hydroxide (5.3 M). AR grade chemicals supplied by Qualigens Chemicals were used for preparing the solutions. The metal ion solutions were pre-mixed in the required stoichiometric ratios and rapidly added to sodium hydroxide solution with intermittent stirring. The pH of the slurry was carefully adjusted at 8 or 8.5. Excess alkali was not used for the precipitation in order to avoid the formation of soluble sodium zincate and thus stoichiometry of the ferrite

precursor. After an aging of 8 h, the precipitate was washed free off nitrate and sodium ions using distilled water. The precipitate was initially dried in air at 80°C for 24 h. The materials were powdered and calcined at 300°C for 36 h. Catalyst pellets of the required mesh size were then obtained by pressing under 10 tonnes of pressure. The catalyst systems were designated as follows: $ZnFe_2O_4$ (ZF-1); $Zn_{0.8}Co_{0.2}Fe_2O_4$ (ZCF-2); $Zn_{0.5}Co_{0.5}Fe_2O_4$ (ZCF-3); $Zn_{0.2}Co_{0.8}Fe_2O_4$ (ZCF-4); $CoFe_2O_4$ (CF-5).

A detailed discussion on the characterization of these materials has been carried out in the previous paper [12]. Phase purity has been evaluated using the powder X-ray diffraction technique, which indicated the exclusive formation of the spinel-phase for all compositions of the systems. The diffuse reflectance infrared spectra (DR-IR) of the samples consist of two distinct broad peaks around 500 and 700 cm^{-1} . In a spinel lattice, every oxygen anion is bonded to three octahedral (Oct.) and one tetrahedral (Tet.) cations [18]. Vibration of the Tet. metal–oxygen group corresponds to the highest restoring force and is thus assigned to the highest frequency band. The band at 500 cm^{-1} indicates the vibration of the Oct. metal–oxygen group [19,20]. Thermal analysis using a TG-DTA instrument (SETARAM-TG-DTA-92) indicated that ferrite systems are thermally stable in the temperature range of 150–1000°C without creating major weight losses, decompositions or phase transformations. Acidity values of the systems follow the following order: CF-5 > ZCF-4 > ZCF-3 > ZCF-2 > ZF-1; basicity values follow exactly the opposite trend (acidity and basicity were qualitatively measured using alcohol dehydration activity of the systems and adsorption experiments using organic molecules having different electron affinity values, respectively [11,12]). The BET surface areas of the different compositions of the systems were determined using an OMNISORP 100 CX instrument; the results are presented in Table 1.

2.2. Activity measurements

The catalytic test was carried out on 3 g of catalyst, retained by inert porcelain beads at almost the center of a vapor-phase down-flow silica reactor (20 mm ID). The materials were pretreated for 12 h at 500°C under oxygen and brought down to the respective

Table 1
Physicochemical characteristics of Zn–Co ferrite systems

<i>x</i>	Cation distribution		Elemental analysis (%) ^a		Surface area ^b (m ² g ⁻¹)
	Tet. site	Oct. site	Zn ²⁺	Co ²⁺	
0	Zn ²⁺	Fe ³⁺	27.0 (27.1)	–	30.0
0.2	Zn _{0.8} ²⁺ Fe _{0.2} ³⁺	Co _{0.2} ²⁺ Fe _{1.8} ³⁺	21.6 (21.8)	4.6 (4.8)	33.6
0.5	Zn _{0.5} ²⁺ Fe _{0.5} ³⁺	Co _{0.5} ²⁺ Fe _{1.5} ³⁺	13.7 (13.8)	12.3 (12.4)	39.5
0.8	Zn _{0.2} ²⁺ Fe _{0.8} ³⁺	Co _{0.8} ²⁺ Fe _{1.2} ³⁺	5.7 (5.5)	20.0 (20.0)	39.8
1.0	Fe ³⁺	Co ²⁺ Fe ³⁺	–	24.7 (24.8)	40.1

^a Quantities in the parentheses indicate the stoichiometric values.

^b Specific surface areas of the samples calcined at 500°C.

reaction temperatures using flowing dry nitrogen. The feed (mixture of aniline and alkylating agent) was delivered using a liquid syringe pump (ISCO — Model 500 D). The reaction products were sampled every 1 h and the aliquots were analyzed by using GC (Shimadzu GC-15A) connected with FID and 2 M, 2% carbowax 20 M+5% KOH on a chromosorb W column. Product characterization was performed by GC-MS and GC-FTIR techniques. The multi-step sequential reaction of methanol or DMC with aniline gives products like NMA, NNDMA and toluidines. Selectivities of the products depend strongly on the alkylating agents; methanol afforded selective *N*-monomethylation whereas DMC gave a mixture of NMA and NNDMA. Selectivity of the product '*i*' is expressed by the equation

$$\text{Selectivity of } i, S_i = \frac{\text{Yield of } i}{\text{Aniline conversion}} \times 100$$

3. Results and discussion

In the case of alkylation of aniline with methanol on Zn–Co ferrites, it has been reported previously [12] that the systems possessing low '*x*' values ($x \leq 0.5$) are selective and active for *N*-monomethylation of aniline leading to NMA. Under optimized conditions, NMA selectivity was better than 98%. Table 2 compares the activities of the systems for aniline alkylation using methanol as the alkylating agent. The optimized condition for the selective formation of NMA was as follows: reaction temperature 325–350°C, methanol to aniline molar ratio 6 and WHSV 2 h⁻¹. All catalysts except ZF-1 displayed excellent stability even

after 10 h (Fig. 1). ZF-1 showed deactivation in the initial period of the run (up to 4 h) and thereafter it maintained a steady value of activity. The deactivation can be due to the normal spinel lattice of ZF-1, where electron hopping is constrained due to the non-availability of reducible cations in the Tet. sites (in ZF-1, Tet. sites are occupied by Zn²⁺ ions, which are highly stable due to their d¹⁰ electronic configuration). 'Co' substitution replaces equivalent amounts of Fe³⁺ ions from Oct. to Tet. sites. Among the systems, ZCF-2 was exceptionally active, selective and stable for *N*-monomethylation of aniline. The stabilization effect of cobalt ions is probably due to the possibility of electron-hopping between tetrahedrally and octahedrally occupied ferric ions, since cobalt ions replace equivalent amounts of Fe³⁺ from Oct. to the neighboring Tet. sites. The presence of Fe³⁺ ions in the Tet. as well as in the Oct. sites facilitates electron delocalization, and thus, the reduced Fe³⁺ ions in the Oct. sites regain their original activity. In ZF-1, since the Tet. sites are occupied solely by inert Zn²⁺ ions, the reduced Fe³⁺ ions cannot regain their original state through redox migration. However, when '*x*' exceeded 0.5, selectivity for NMA decreased owing to the deamination of aniline on the strong acidic centers created by Co²⁺ ions. The large quantity of benzene and toluene over these systems accounts for the conclusion. This suggests that, for the methylation of aniline with methanol over the Zn–Co ferrites, the Fe³⁺ ions in the Oct. sites are mainly responsible for the activity of the system, whereas Co²⁺ ions in low concentration stabilize the spinel matrix during the reaction. Fe³⁺ ions provide moderate acid strength for the surface, whereas replacement of Fe³⁺ ions by Co²⁺ ions creates strong acidic sites, where aniline

Table 2
Aniline alkylation using methanol as the alkylating agent — effect of reaction temperature^a

Reaction temperature (°C)	Aniline conversion	NMA yield (%)	NMA selectivity (%)	NNDMA yield (%)	Benzene+toluene yield (%)
ZF-1					
250	14.4	14.1	97.9	–	0.3
300	56.0	55.1	98.5	–	0.8
350	79.6	71.4	91.4	7.1	1.0
400	57.7	51.1	88.4	5.4	1.3
ZCF-2					
300	55.8	54.3	97.0	1.3	0.5
350	73.8	67.1	93.9	5.4	1.3
400	58.3	51.0	88.4	5.5	2.0
ZCF-3					
250	7.8	7.1	90.7	–	0.5
300	42.1	38.4	91.3	1.8	1.2
350	57.1	44.8	78.4	9.9	2.2
400	49.2	37.6	76.5	7.2	3.4
ZCF-4					
250	11.2	5.7	51.3	–	5.4
300	36.3	20.4	56.5	2.0	13.6
350	48.0	24.4	50.9	4.2	19.2
400	44.3	17.8	40.1	5.8	20.2
CF-5					
250	23.8	3.0	12.7	0.5	20.2
300	49.2	8.1	16.4	2.0	39.0
350	53.5	7.4	13.9	4.0	42.0
400	54.1	4.4	8.1	4.1	45.5

^a Methanol to aniline molar ratio, 6, WHSV, 2 h⁻¹, TOS, 1 h.

undergoes decomposition due its strong interaction with the surface.

Since Zn_{1-x}Co_xFe₂O₄ type systems are selective and active for *N*-monomethylation of aniline using methanol, a similar study has been done using DMC as the alkylating agent. Table 3 shows the activities and selectivities of various compositions of the system in methylation of aniline with DMC. In contrast to methylation with methanol, every catalyst gave both mono- and di-*N*-alkylated products. As ‘*x*’ increased, more NNDMA was formed. ZF-1 and ZCF-2 performed nearly the same activities and both these systems afforded more NMA. Ring methylation did not occur at all under the reaction conditions studied. Aniline conversion increased progressively with increase in the ‘*x*’ value; however, selectivity of higher members (*x*>0.5) was much lower than in the more Zn-substituted systems. The similarity of aniline conversion and total alkylation (both *N*-mono- and

N,N-di-alkylations) activity pattern using methanol and DMC suggests the involvement of the same active sites of the catalyst surface, irrespective of the alkylating agent. However, the considerable differences in the yield and selectivities of the respective products over the same catalyst suggest that the adsorbed active alkylating species formed from methanol and from DMC are different. Aniline alkylation over oxide surface involves a concerted mechanism, as suggested by Al Nanko et al. [21]. Optimum concentration of acid–base centers is needed for adsorption and subsequent polarization of both aniline and the alkylating agent. However, since aniline is a strong base, it can easily coordinate even with weak acid centers. Hence, it is the change in the basicity of the system, rather than the acidity, that controls the overall performance of the catalysts. We have reported that cobalt addition in Zn-ferrite increased the acidity with a simultaneous decrease in the basicity of the system. Thus, the low

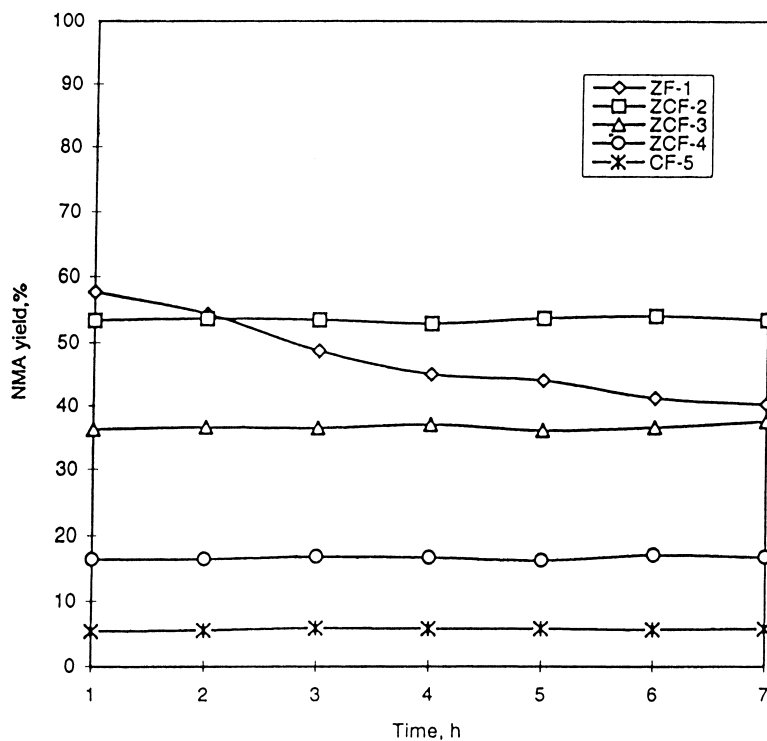


Fig. 1. Effect of time-on-stream (TOS): WHSV, 2 h^{-1} ; reaction temperature, 350°C ; methanol to aniline molar ratio, 2. Concentration of *N*-methylaniline is plotted as a function of reaction time in hours.

activity on cobalt substitution can be explained as being due to the removal of basic centers originally present on ZF-1 by cobalt substitution. Due to the lower coordination number of the tetrahedral cations, the effective attractive force for a single Tet. M–O bond will be strong [22]. Since each Oct. cation is surrounded by more anions, the Oct. M–O bond will be weaker, and thus, the bonding will be more polar.

Probing the surface layer of materials has become more accurate after researchers introduced the low energy ion scattering (LEIS) technique in the catalytic field. Jacobs et al. [23] applied this technique to evaluate spinel surface composition and revealed that most of the surface sites are octahedral; thus, octahedral cations play an important role in the catalytic activity. Thus, it is reasonable to conclude that, in the adsorp-

Table 3

Aniline conversion and selectivity data of aniline methylation using DMC over different Zn–Co ferrites^a

Catalyst composition	Product distribution (wt.%)			
	Aniline conversion	NMA selectivity	NNDMA selectivity	Others ^b
ZF-1	50.0	75.3	10.9	13.8
ZCF-2	50.5	73.8	11.9	14.2
ZCF-3	55.5	67.2	16.0	16.9
ZCF-4	57.6	62.2	20.1	17.7
CF-5	60.1	61.2	21.9	17.0

^a Reaction temperature, 250°C ; WHSV, 1.2 h^{-1} ; molar ratio (DMC to aniline), 2; TOS, 1 h.

^b Others include DMC fractions, benzene, toluene and traces of unidentified products.

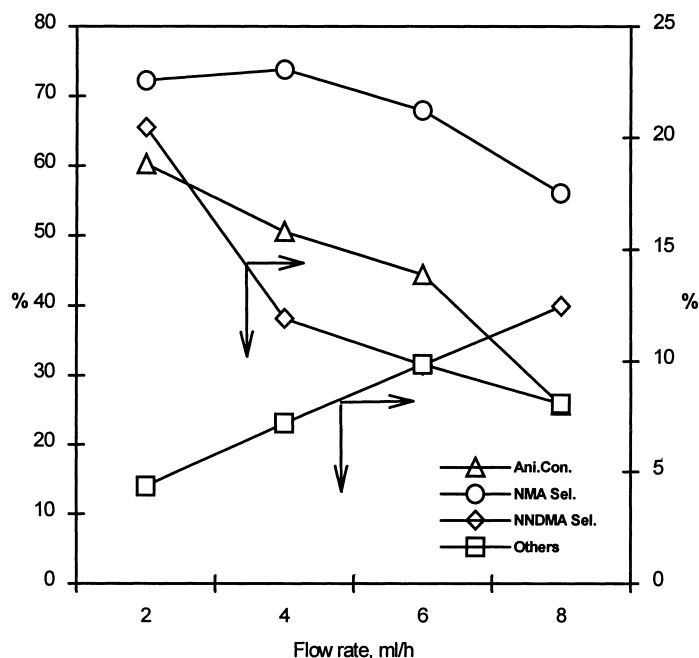


Fig. 2. Effect of flow rate on conversion and selectivities over ZCF-2. Reaction temperature, 250°C; molar ratio (DMC to aniline), 2; TOS, 1 h.

tion and subsequent reaction of aniline and DMC, the $\text{Fe}_{\text{Oct}}^{3+}/\text{Co}_{\text{Oct}}^{2+}$ ratio of the systems is an important factor. As the ratio decreases, acidity increases, resulting in a sharp variation in the selectivity pattern.

In order to understand the influence of various process parameters, further studies have been performed using ZCF-2 as a model system.

A series of experiments were performed in the temperature range of 200–300°C using a feed composition (DMC/aniline) of 2 and WHSV of 1.2 h⁻¹. Unlike the experiments using methanol, here, the temperature showed a marked influence on selectivities of the products. At low temperature, NMA selectivity was high, but it decreased quickly with increase in temperature. Increase in temperature increased the *N,N*-dialkylation rate up to 280°C and thereafter it suddenly decreased. The other products include DMC fractions, benzene and toluene. The results are summarized in Table 3. Increase in temperature above 280°C increased the decomposition rate of DMC substantially, and above 300°C, conversion of DMC fractions exceeded 35%.

The effects of DMC/aniline molar ratio on the conversion of aniline and on the yields of various prod-

ucts were studied. At low DMC concentrations, the selectivities of NMA and NNDMA were nearly 74 and 12%. At high DMC/aniline ratio, more NNDMA was formed. When the ratio was 4, the selectivity of NMA was about 40%, whereas that of NNDMA was increased up to 28%.

The optimum feed flow rate for NMA formation was 4 ml h⁻¹ (WHSV 1.2 h⁻¹). At low flow rate, more NNDMA was formed due to the long contact time with the catalyst. At sufficiently high flow rate, aniline conversion and alkylation activity diminished. The results are shown in Fig. 2.

The above discussion clearly indicates that DMC can act as an effective *N*-alkylating agent at sufficiently low temperature, where methanol shows only mild activity. However, unlike methanol, DMC afforded both mono- and di-substitution on nitrogen, leading to less selectivity for NMA. A comparison of various aspects of aniline alkylation using methanol and DMC over ZCF-2 is made in Fig. 3. It is interesting to note the greater amount of *N,N*-dialkylated product at sufficiently low temperature where methanol afforded nearly 99% NMA selectivity. This result is contrary

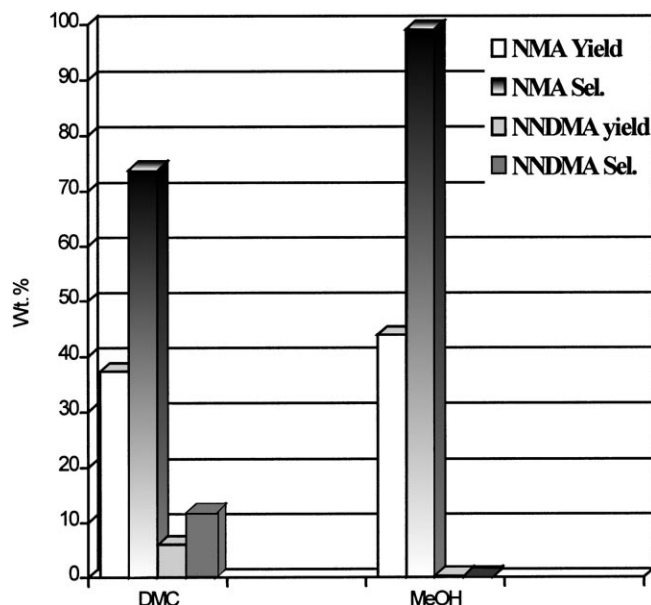


Fig. 3. A comparison of aniline alkylation using methanol and DMC over ZCF-2. In both cases, the molar ratio (alkylating agent to aniline) was maintained at 2. Reaction temperature for alkylation using methanol, 350°C, for alkylation using DMC, 250°C; catalyst amount 3 g; feed flow rate for alkylation using methanol, 4 ml h⁻¹, for alkylation using DMC, 2 ml h⁻¹.

to that obtained for systems like Al₂O₃, MgO [24] and alkali-exchanged EMT zeolites [25], because such systems show higher selectivity for NMA when using DMC than when using methanol.

4. Conclusions

The catalyst compositions of the Zn_{1-x}Co_xFe₂O₄ ($x=0, 0.2, 0.5, 0.8$ and 1.0) series possessing ‘ x ’ values, $x \leq 0.5$, are active for *N*-methylation of aniline, using DMC as the alkylating agent. Higher activity was observed in the temperature range of 200–300°C. However, unlike the experiments using methanol for alkylation, DMC afforded both mono- and di-substitution on the nitrogen of aniline, leading to comparatively lower selectivity for NMA. Increase in the temperature as well as the molar ratio (DMC/aniline) increased the dialkylation rate. The main advantage of the reaction is that alkylation is possible at sufficiently low temperature where methanol cannot work properly. Both NMA yield and selectivity were higher for the reaction using methanol, even though high activity was observed in

the temperature range of 325–350°C. In both cases, alkylation activity follows a similar trend with respect to the composition of the ferrosipinel system, indicating the participation of same active group of the catalyst in the two sets of experiments. However, the considerable difference in the yield as well as the selectivity of the products suggests that the active alkylating species formed after the adsorption of methanol and DMC may be different.

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References

- [1] S. Narayanan, V. Durgakumari, A. Sudhakar Rao, Appl. Catal. A 111 (1994) 133.
- [2] P.R. Hariprasad Rao, P. Massiani, D. Barthomeuf, Catal. Lett. 31 (1995) 115.
- [3] Y. KiPark, K. YonPark, I. Woo, Catal. Lett. 26 (1994) 169.

- [4] W.W. Kaeding, R.E. Holland, *J. Catal.* 109 (1988) 212.
- [5] A.G. Hill, J.H. Ship, A.J. Hill, *Ind. Eng. Chem.* 43 (1951) 1579.
- [6] O. Oanaka, K. Ishikawa, Y. Isumi, *Chem. Lett.* (1992) 1783.
- [7] A.N. Ko, C.L. Yang, W. Zhu, H. Lin, *Appl. Catal. A* 134 (1996) 53.
- [8] F.M. Bautista, J.M. Campelo, A. Garcla, D. Luna, J.M. Marrinas, A.A. Romero, *Appl. Catal. A* 166 (1998) 39.
- [9] F.M. Bautista, J.M. Campelo, A. Garcla, D. Luna, J.M. Marrinas, A.A. Romero, M.R. Urbano, *J. Catal.* 172 (1997) 103.
- [10] H. Matsushasi, K. Arata, *Bull. Chem. Soc. Jpn.* 64 (1991) 2605.
- [11] K. Sreekumar, T. Raja, B.P. Kiran, S. Sugunan, B.S. Rao, *Appl. Catal. A* 182 (1999) 327.
- [12] K. Sreekumar, T.M. Jyothi, M.B. Talawar, B.S. Rao, S. Sugunan, *J. Mol. Catal.*, in press.
- [13] Z.H. Fu, Y. Ono, *Catal. Lett.* 22 (1993) 442.
- [14] Z.H. Fu, Y. Ono, *Catal. Lett.* 18 (1993) 59.
- [15] F. Trotta, P. Tundo, G. Moraglio, *J. Org. Chem.* 52 (1987) 1300.
- [16] Y. Ono, *Cat. Tech.* (1997) 35.
- [17] P.S. Anilkumar, J.J. Schotri, S.D. Kulkarni, C.E. Deshpande, S.K. Date, *Mater. Lett.* 27 (1996) 293.
- [18] F.C. Romeijn, *Philos. Res. Rep.* 8 (1953) 304.
- [19] R.D. Waldren, *Phys. Rev.* 99 (1955) 1927.
- [20] M.P. White, B.A. De Angelies, *Spectrochim. Acta A* 23 (1967) 985.
- [21] A. Nanko, C.L. Yang, W. Zhu, H. Lin, *Appl. Catal. A* 134 (1996) 53.
- [22] C.S. Narasimhan, C.S. Swamy, *Appl. Catal.* 2 (1982) 315.
- [23] J.P. Jacobs, A. Maltha, J.R.H. Reintjes, T. Drimal, V. Ponec, H.H. Brogersma, *J. Catal.* 147 (1994) 294.
- [24] Y. Ono, *Cat. Tech.* (1997) 35.
- [25] P.R.P. Rao, P. Massiani, D. Barthomeuf, *Catal. Lett.* 31 (1995) 115.