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Gas-phase hydroxylation of benzene over H–Ga-FER zeolite

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The direct hydroxylation of benzene with N_2O is studied using H–Ga-FER zeolite as catalyst. The H–Ga-FER zeolite was synthesized by using the hydrothermal synthesis route. Pyrrolidine was used as a template. The catalyst was characterized by using XRD and NMR techniques. The gas-phase hydroxylation reaction was carried out using nitrous oxide gas as an oxidant. The reaction was thoroughly studied by changing different parameters like temperature, time, reactant mole ratio and contact time (WHSV). It was observed that by using H–Ga-FER, phenol was formed with 100% selectivity. The deactivation is faster in case of H–Ga-FER as compared with Al-FER and Fe-FER.

Keywords: H–Ga-FER, N_2O, hydroxylation

1. Introduction

So far the cumene process is most widely used for the production of phenol [1]. An alternative route by direct hydroxylation of benzene was explored by researchers. Heterogeneous catalysts played an important role during this search. Hölderich et al. [2] reported liquid-phase synthesis of phenol using H_2O_2 in the presence of TS-1. Iwamoto et al. [3] explored the gas-phase synthesis of phenol using N_2O in presence of a V_2O_5/SiO_2 catalyst. Several researchers have carried out gas-phase synthesis of phenol using N_2O as oxidant and analogs of ZSM-5 zeolite as a catalyst [4–23]. In the present work we report gas-phase hydroxylation of benzene over a H–Ga-FER catalyst where selective phenol formation is observed. The catalyst is prepared by reported procedures [24].

2. Experimental

2.1. Synthesis

The H–Ga-FER catalyst which was used in the reaction was synthesized by isomorphous substitution of gallium in place of Al in ferrierite zeolite using the following hydrothermal synthesis route.

Typical synthesis included addition of a solution prepared by mixing 1.625 g of $Ga_2(SO_4)_3$ (Aldrich) in 30 g of distilled water and 1.8 g of concentrated H_2SO_4 (98%, S.D. Fine Chemicals) in 10 g of distilled water to 52.5 g of Na_2SiO_3 (28% SiO_2, 9% Na_2O) in 40 g distilled water. Then, 10 g template pyrrolidine was added to the gel mixture and the gel was stirred for approximately 1 h. The final gel pH was 11.5 ± 0.2. The gel was transferred to a 300 ml stainless-steel autoclave (Parr 4861, 300 ml) and heated at 433 K for 40 h. The autoclave was quenched with cold water. The material was filtered, washed and dried at 373 K. Utmost care was taken to clean the autoclave to avoid any seeding effect from the previous batches. Samples with different SiO_2/Ga_2O_3 ratios were synthesized. The initial gel composition was

$$27.18Na_2O : 32Py : (30\text{–}100)SiO_2 : 1Ga_2O_3 : 4.97H_2SO_4 : 1798H_2O,$$

where Py = pyrrolidine.

The as-synthesized Ga-FER samples were calcined at 773 K for 10–12 h to convert them into the sodium form and then into the ammonium form by multiple exchanges with 2 M ammonium nitrate solution at 363 K. The ammonium form was dried at 383 K and then calcined in a step-wise mode at 753 K to obtain the H^+ form.

2.2. Characterization

The solid Ga-FER catalyst obtained was characterized by X-ray powder diffraction (Rigaku D Max III VC) using Cu K_α radiation. The chemical analyses of the samples were carried out by XRF (Rigaku 3070 X-ray spectrometer). The samples were characterized by an MAS NMR instrument (Bruker MSL-300) for ^{71}Ga and ^{29}Si nucleus.

2.3. Catalysis

The catalytic reactions were carried out in a standard fixed-bed down-flow reactor system at various temperatures at atmospheric pressure. The products were analyzed on a Shimadzu gas chromatograph using a FAPS packed column.

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3. Results and discussion

Two Ga-FER samples of different Si/Ga ratios were synthesized (table 1). The gallium incorporation in the ferrierite lattice was indicated by the unit cell parameters of the Ga-FER and the corresponding Al-FER. There is an increase of 44 Å^3 in the unit cell volume of the ferrierite due to incorporation of the slightly bulkier Ga^{3+} ion in place of Al^{3+} (table 1, sample 1).

Figure 1(A) shows the XRD patterns of the Ga-FER samples at different synthesis times. Figure 1(B) shows the synthesis kinetics of Ga-FER. The Ga-FER was synthesized at 160 °C for different times (10, 20, 30 and 40 h). The highest peak intensities were plotted against time. It gives a typical "S" curve, which is characteristic of zeolite synthesis.

Figure 2(A) shows the ^{71}Ga MAS NMR spectra of Ga-FER (samples 1 and 2). The sharp peak at 150 ppm indicates the presence of tetrahedraly coordinated framework Ga^{3+} species [25–28]. Figure 2(B) shows the ^{29}Si MAS NMR of the Ga-FER samples. The signal at -110 ppm is due to the Si (0Ga 4Si) co-ordination and the signal at -102 ppm can be assigned to the Si (1Ga 3Si) co-ordination [29]. Both these NMR results confirm the Ga incorporation into the ferrierite framework which is also confirmed by unit cell expansion.

The gas-phase hydroxylation of benzene was carried out on the above synthesized catalysts. Penov et al. [12,13] have suggested the following reaction mechanism:

$$N_2O \rightarrow (O) + N_2 \qquad (1)$$

$$C_6H_6 + (O) \rightarrow (C_6H_5OH) \qquad (2)$$

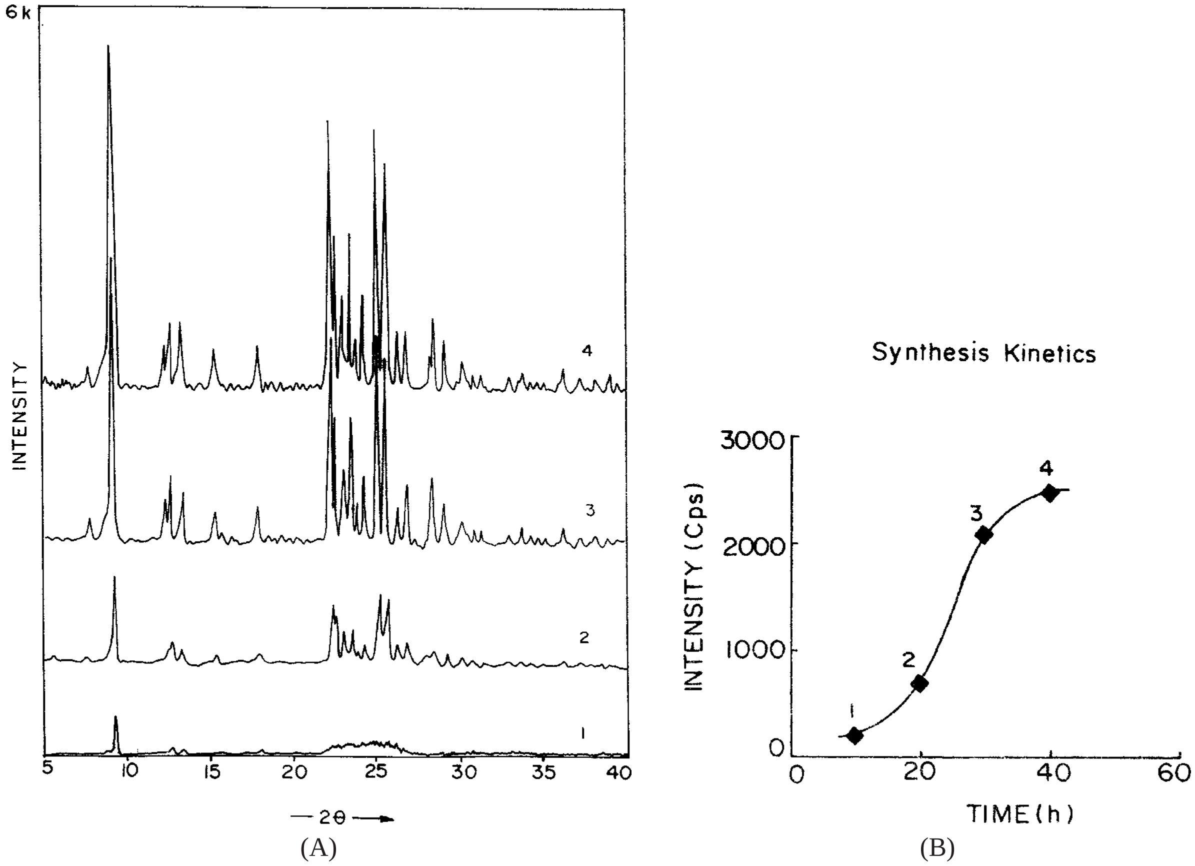
$$(C_6H_5OH) \rightarrow C_6H_5OH \qquad (3)$$

Species in parentheses are the active species.

Table 1
Chemical analysis and XRD data.

Sample	Si/Ga		Ga	Unit cell parameters (Å)			Unit cell
	Input gel	Product (by XRF)	(wt%)	a_0	b_0	c_0	volume (Å^3)
Sample 1 (Ga-FER)	32	19.8	5.44	18.96	14.14	7.47	2002.12
Sample 2 (Ga-FER)	15	9.9	10.14	–	–	–	–
Sample 3 (Ga-impregnated Al-FER)	–	17[a]	5.44	–	–	–	–
Al-FER	–	17[a]	–	18.69	14.06	7.40	1958.00

[a] Si/Al.



(A) (B)

Figure 1. XRD spectra of the Ga-FER catalyst at different time: (1) 10, (2) 20, (3) 30 and (4) 40 h.

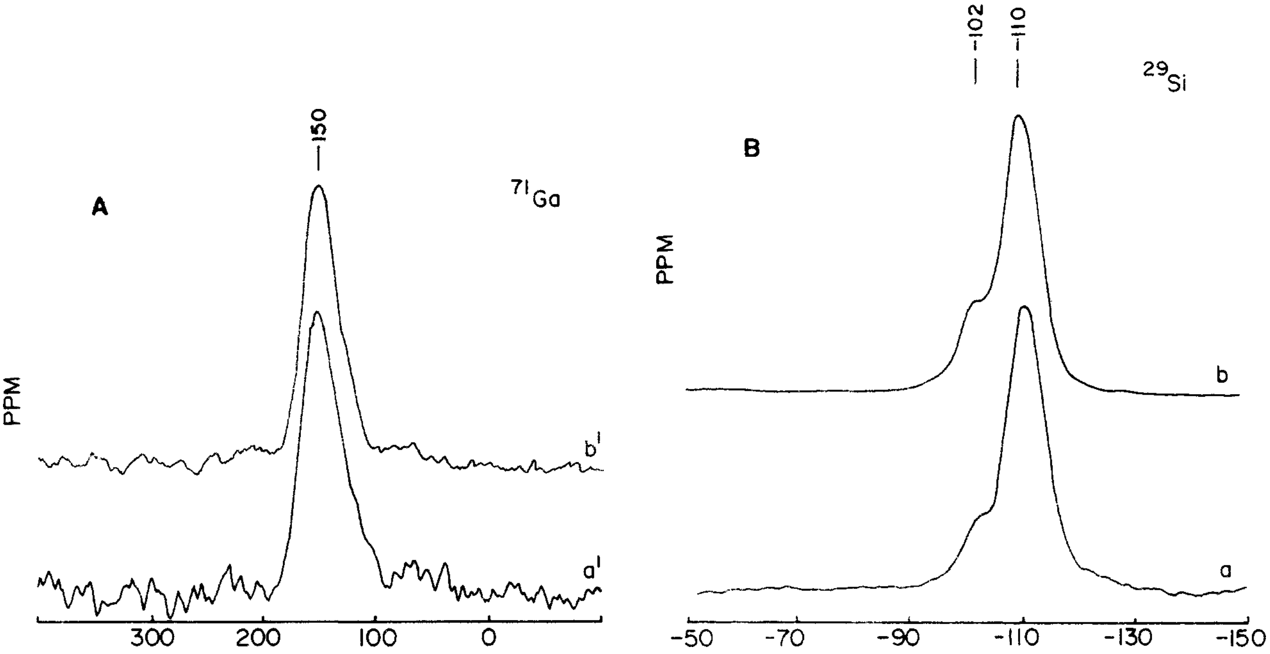


Figure 2. MAS NMR of the Ga-FER catalyst: (a, a′) sample 1 and (b, b′) sample 2.

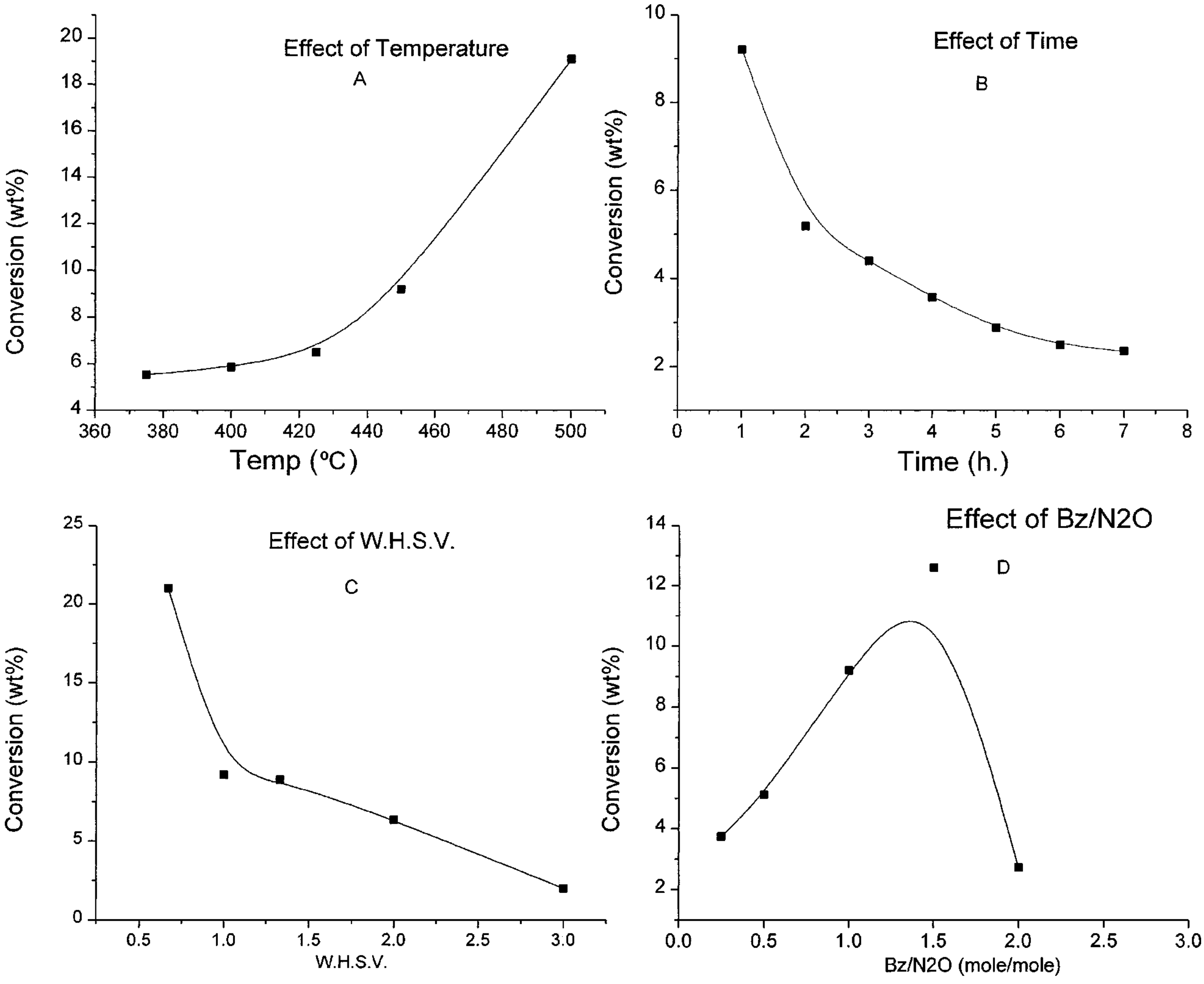


Figure 3. Effect of various parameters on the gas-phase hydroxylation of benzene.

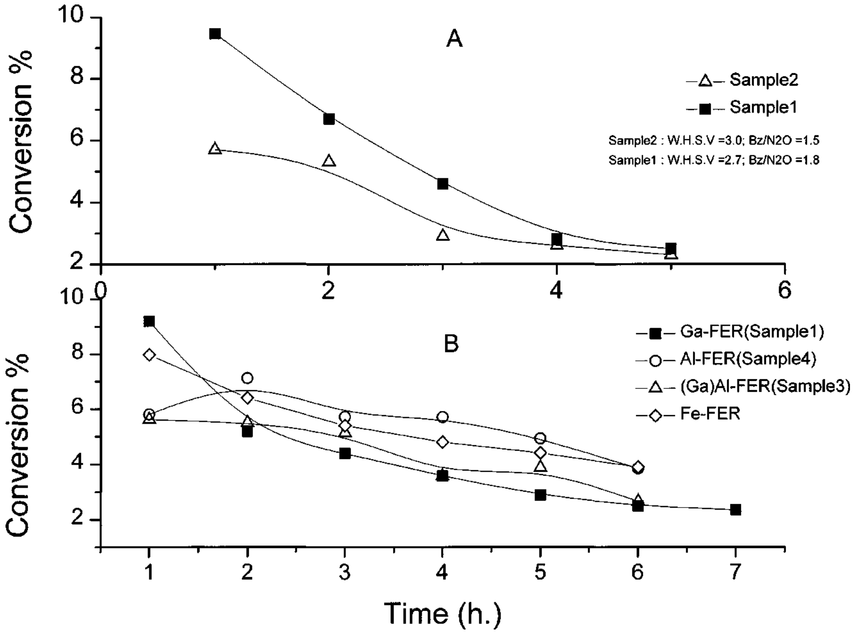


Figure 4. Effect of gallium content on the gas-phase hydroxylation of benzene.

The α-oxygen (O) species acts as oxidant in the above reaction. The (O) species was generated on the very special type of α-surface species on Ga-FER. These sites are essential for the hydroxylation reaction [13], and, hence, only the catalysts with α-sites are active for this reaction. The reaction was exothermic. H–Ga-FER facilitated high selectivity to phenol in the reaction product.

Figure 3(A) shows the effect of temperature on the benzene conversion. As expected, the conversion increases with temperature. At 300 °C the conversion was 5.59% which increased to 19.1% at 500 °C.

The effect of time is shown in figure 3(B). The catalyst deactivation is fast. The conversion of benzene decreased from 9.2% at 1 h to 2% in 7 h. The catalyst deactivation was due to coke formation. The coke was the high boiling polymeric material which was strongly adsorbed on the catalyst.

Figure 3(C) represents the effect of WHSV (contact time). At very high contact time (low WHSV $= 0.67$) the conversion was 21%, which was decreased to 2.0% at very low contact time (high WHSV $= 3.0$).

The effect of benzene/N_2O mole ratio is shown in figure 3(D). The conversion was increased from 3.75% at 0.25 ratio to 12.6% at 0.67 ratio. Again it was decreased to 2.78% at ratio 2.0. It indicates that at $Bz/N_2O = 0.67$, the probability of the second step in the above mechanism is more favored.

Figure 4(A) shows the effect of Ga content on the benzene conversion. The gallium content of sample 2 (10.14%) was more than that of sample 1 (5.44%). The high activity of sample 1 may be due to the better dispersion of tetrahedral Ga^{3+} species acting as active α-species in sample 1 than that of 2.

Figure 4(B) gives the comparison between the Ga-FER, Ga-impregnated Al-FER, Fe-FER and Al-FER. Initially the activity of Ga-FER was more (9.2%) compared to Al-FER (5.81%), Ga-impregnated Al-FER (5.62%) and Fe-FER (7.98%). This may be due to the presence of a greater number of active α-species in purely isomorphous substituted Ga-FER (sample 1) than in the same quantity of gallium-impregnated Al-FER and pure Al-FER. The rate of deactivation of Ga-FER was more than that of Al-FER. When compared with Fe-FER it was observed that the rate of deactivation was high in Ga-FER. However, the activity in terms of conversion of benzene was high at 450 °C for Ga-FER.

4. Conclusion

The gallium analog of Al-FER was synthesized having gallium in the zeolite framework. The tetrahedral Ga species was proved by ^{71}Ga MAS NMR techniques. The expansion in the unit cell volume confirms the gallium incorporation.

The synthesized Ga-FER catalyst was tested in gas-phase hydroxylation of benzene using N_2O as oxidant. Ga-FER is very active at high temperature (500 °C) and high contact time (low WHSV). The catalyst deactivation was very rapid. It was found that the well dispersed tetrahedral gallium species was acting as a more active center in the reaction than the impregnated octahedral gallium species. Ga-FER deactivates very rapidly as compared to Al-FER and Fe-FER.

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