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Phenol Alkylation with Methanol on Oxide and Zeolite Catalysts

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Introduction

The alkylation of phenol with methanol received greater practical importance after the use of 2,6-xylenol as a monomer for polyphenylenoxides, resistant to high temperature and pressure [1–5]. Among the industrially used catalysts for the synthesis of 2,6-xylenol gamma-alumina [2, 6, 7] and Fe–V–O/SiO₂ [1] are recommended. The activity of iron catalysts modified with chromium, silicon, potassium or cesium ions [4] and of the system V₂O₅–Cr₂O₃ [5] has been investigated recently. It has been established that SiO₂ stabilized the structure of Fe₂O₃ [4].

The possibility to obtain O- or C-alkylation products by phenol alkylation and the easy conversion of anisol into ortho-cresol emphasized the role of the phenol adsorption mode and of the basic sites of the catalyst on the reaction selectivity [8]. The aim of our study was to compare the activity and selectivity of different oxide catalysts in phenol methylation. The acid-base properties of these catalysts were checked by the cyclohexanol test [9]. The Broensted acid sites of the catalysts activated the dehydration of cyclohexanol to cyclohexene, while the basic sites participated in dehydrogenation to cyclohexanone.

In accordance with the literature data [2], we found that the shape-selective zeolites of the type HZSM-5 lead to the methylation of phenol to anisol and ortho-cresol. The formation of 2,6-xylenol was suppressed and probably the less bulky 2,4- and 2,5-xylenol were obtained [10]. The opportunity for selectivity changes by adding some oxides to the zeolites has been investigated, too.

Experimental

ZnO, Fe₂O₃ and V₂O₅ were reagent grade commercial products. MgO was obtained from MgCO₃ by calcination at 803 K. Mn₃O₄ was prepared by MnCO₃ \cdot Mn(OH)₂ \cdot nH₂O decomposition at 803 K and identified by IR spectra [11]. Zeolites ZSM-5 with different molar ratios of Si/Al were synthesized from alkali solutions of alumina and silica in the presence of tetrapropyl ammonium bromide as a template. The zeolite structure has been characterized by X-ray diffraction, raster electron microscopy and IR spectra [12]. The alkylation experiments were performed in a fixed bed flow reactor at atmospheric pressure. The catalyst /4 g/ was pressed, crushed and sieved to particles of 1.25–2.5 mm. Its activation and regeneration was conducted at 773 K under air flow. Before the alkylation experiment the catalyst was flushed with argon ensuring an inert atmosphere for the catalytic reaction.

The mixture of methanol and phenol in molar ratio 5:1 was introduced into the reactor via calibrated syringe and evaporator.

The reaction products were analyzed by GC using a FID and a 2 m column with 15 % DC 550 on Chromosorb W 60-80 mesh at 403 K. Gaseous products (C_2-C_4 hydrocarbons) formed at higher temperature from methanol, taken in excess. In some cases polyalkylphenols were also formed.

Results and Discussion

The comparison of MgO, ZnO and Fe_2O_3 in phenol methylation (Fig. 1 and 2) showed the advantages to use Fe_2O_3 as a catalyst, giving a considerable phenol conversion and a significant ortho-cresol selectivity at lower temperature (Fig. 2). The



Fig. 1 Alkylation of phenol with methanol (1:5 moles), LHSV 1.75 hour⁻¹, on MgO (\triangle), ZnO (\Box), Fe₂O₃ (\bigcirc): dark points – yield of liquid products, wt %; open points – phenol conversion



Fig. 2 Selectivity to o-cresol (open points) and 2,6-xylenol (dark points) in the presence of MgO (\triangle , ZnO (\square , Fe₂O₃ (\bigcirc); \triangle – anisol on MgO

activity of MgO at higher temperature must be emphasized. The low activity of ZnO was compensated by higher selectivity to ortho-cresol (Fig. 2). Only in the presence of MgO (Fig. 2), anisol has been also formed. Fe₂O₃ was the best catalyst for 2,6-xylenol production.

The selectivity to 2,6-xylenol of mechanical mixture of MgO + ZnO (9:1 weight ratio) was better than the individual oxides (Fig. 3) by increased phenol conversion.



Fig. 3 Yield of liquid products (\bigcirc), phenol conversion (\bigcirc), o-cresol (\square) and 2,6-xylenol (\blacksquare) selectivity on MgO + ZnO (9:1 weight ratio)

Tanabe has shown [8] that the selectivity in phenol methylation depends on the acid and base properties of the catalyst used. The base properties of MgO have been demonstrated by its ability to dehydrogenate cyclohexanol to cyclohexanone [9], while under the same conditions ZnO and Fe₂O₃ showed an amphoteric character. The existence of basic sites favored the formation of anisol and ortho-cresol (Fig. 2), while additional acid sites are important in the synthesis of o-cresol and 2,6-xylenol. Tanabe suggested a specific mode of phenol adsorption on MgO, favoring the formation of anisol and o-cresol.

The industrial application of Fe_2O_3 in 2,6-xylenol synthesis is evident from the literataure [1, 4] in spite to the ability of Fe_2O_3 to decompose methanol under the reaction conditions [13]. But



Fig. 4 Yield of liquid products (\bigcirc), phenol conversion (\bigcirc), o-cresol (\square) and 2,6-xylenol (\triangle) selectivity of HZSM-5 (Si/Al = 500) + V₂O₅ (9:1 weight ratio), LHSV 3.5 hour⁻¹

Fe₂O₃ is used together with the highly acidic V₂O₅ [1, 9]. We found that due to easy reduction and sintering, described also in the literature [14] V₂O₅ cannot be used alone as alkylation catalyst. Taking into account the stabilizing role of SiO₂ [4] we investigated the influence of a zeolite on the activity and selectivity of V₂O₅ in phenol methylation (Fig. 4). The advantage of the catalytic system is the increased selectivity in o-cresol and 2,6-xylenol production, compared with some other modifications of HZSM-5 zeolites with oxides [10, 15].

Another investigated catalyst consisted of combination between a zeolite and the preliminary studied Mn_3O_4 [11]. The results from the cyclohexanol test with Mn_3O_4 [9] permitted its combination with a ZHSM-5 zeolite with higher content of aluminium, i.e. higher concentration of Broensted acid sites. The dependence of phenol conversion on the amount of Mn_3O_4 in the catalyst (Fig. 5) demonstrated its poisoning effect on the zeolite activity.



Fig. 5 Yield of liquid products (\bigcirc), phenol conversion (\bigcirc), o-cresol (\bigcirc) and 2,6-xylenol (\bigcirc) selectivity on mixtures of HZSM-5 (Si/A1 = 100) + Mn₃O₄, 673 K, LHSV 3.5 hour⁻¹, methanol:phenol = 5 (moles)

A catalyst containing HZSM-5 zeolite and Mn_3O_4 (1:1 weight ratio) at 673 K showed very high selectivity in o-cresol production (Fig. 5 and 6). Increased temperatures favored the phenol conversion, but also the high selectivity to 2,6-xylenol. The observed changes in the selectivities to o-cresol and 2,6-xylenol confirmed the intermediate role of o-cresol in 2,6-xylenol formation.



Fig. 6 Yield of liquid products (\bigcirc), phenol conversion (\bigcirc), o-cresol (\bigcirc) and 2,6-xylenol (\bigcirc) selectivities on HZSM-5 (Si/Al = 100) + Mn₃O₄ (1:1 weight ratio), LHSV 3.5 h⁻¹

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