

Reductive etherification of furfural on the mixture of Cu/Al₂O₃ catalyst prepared from copper ammonia complex and ZSM-5-Al₂O₃

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REDUCTIVE ETHERIFICATION OF FURFURYL WITH ISOPROPANOL OVER GRANULATED CATALYSTS

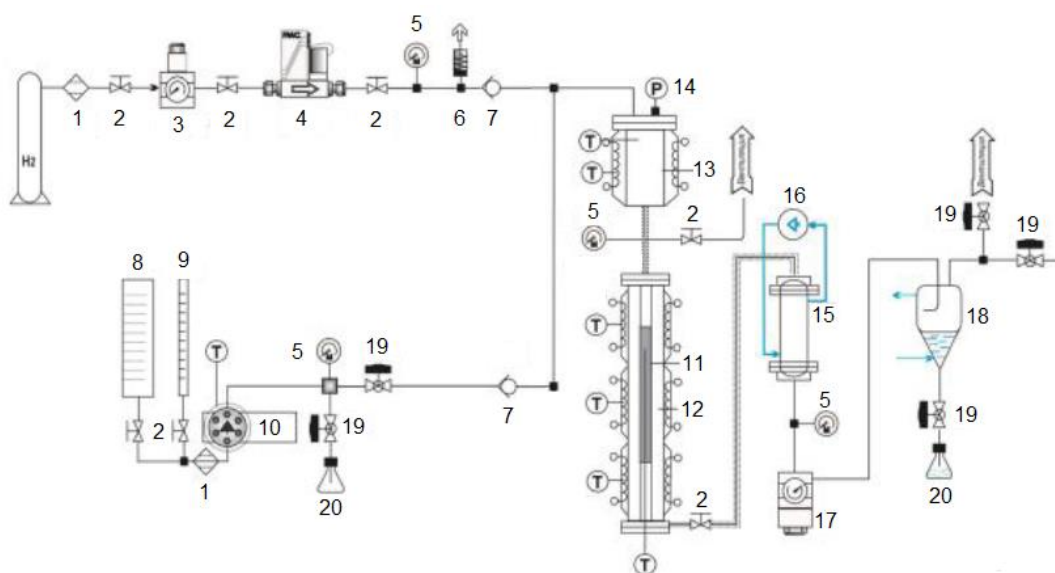


Fig. SI-1. Setup for reductive etherification of furfural with isopropanol over the granulated Cu/Al₂O₃ catalyst in combination with-ZSM-5(40)-Al₂O₃.

1 – filter, 2 – shut-off valve, 3 – downstream pressure regulator, 4 – gas flow controller, 5 – pressure gauge, 6 – safety valve, 7 – check valve, 8 – raw material tank, 9 – measuring tank, 10 – liquid pump, 11 – tubular reactor, 12 – reactor furnace, 13 – mixer, 14 – pressure sensor, 15 –

condenser, 16 – cryostat, 17 – back-pressure regulator, 18 – high-pressure separator, 19 – control valve, 20 – receiving flask

NH₃-TPD TECHNIQUE

The ammonia sorption capacity of the zeolite-Al₂O₃ samples were investigated using the temperature-programmed desorption of ammonia (NH₃-TPD). Figure SI-1 shows the NH₃-TPD profiles for a series of ZSM-5(*x*)-Al₂O₃ composites in comparison with the Al₂O₃ profile normalized to its content in the composite (70 wt%). Two temperature regions can be distinguished on the NH₃-TPD curves: low-temperature (below 350°C, LT) and high-temperature (above 350 °C, HT).

The LT range of composites differs little from the corresponding part of the Al₂O₃ profile. This region corresponds to ammonia, which is desorbed from weak acid sites localized mainly on the surface of Al₂O₃. At temperatures above 350 °C, the NH₃-TPD curves of the ZSM-5(*x*)-Al₂O₃ samples contain one broad asymmetric peak, which is a superposition of several peaks associated with desorption of ammonia from strong acid sites. Desorption at temperatures above 600°C can be associated with amination of the alumina surface and dehydroxylation of the zeolite. Therefore, the concentrations of strong acid sites of ZSM-5(*x*)-Al₂O₃ were estimated by integrating the NH₃ desorption peak in the temperature range of 350–560 °C [S1].

The intensity of the HT peak decreases with an increase in the Si/Al ratio of the zeolite from 15 to 140 indicating a decrease in the number of strong acid sites in ZSM-5(*x*)-Al₂O₃ (Table SI-1). The HT part of the NH₃-TPD profiles of the ZSM-5(140)-Al₂O₃ and Al₂O₃ is almost identical (Figure SI-1).

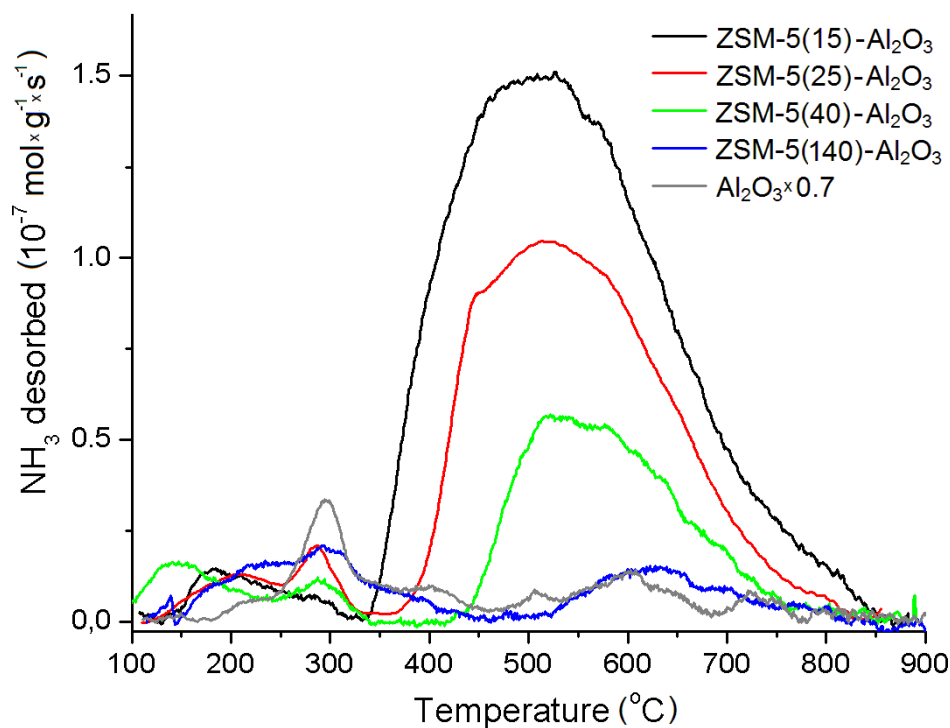


Fig. SI-2. NH₃-TPD profiles of ZSM-5(*x*)-Al₂O₃ composites and Al₂O₃.

Table SI-1. Acidic properties of ZSM-5(*x*)-Al₂O₃ composites measured by NH₃-TPD [S1].

Composite	Concentration of acid sites (μmol g ⁻¹) from which ammonia desorbed at				Total concentration of acid sites (μmol g ⁻¹)
	<400 °C	420–490 °C	530–560 °C	>600 °C	350–560 °C
ZSM-5(15)-Al ₂ O ₃	11	73	71	103	155±20
ZSM-5(25)-Al ₂ O ₃	-	39	65	49	104±10
ZSM-5(40)-Al ₂ O ₃	-	16	23	27	39±5
ZSM-5(140)-Al ₂ O ₃	-	-	3	12	3±1
Al ₂ O ₃	-	-	2	13	2±1

FT-IR SPECTROSCOPY

Surface acid sites of ZSM-5(*x*)-Al₂O₃ composites and Al₂O₃ were also characterized by FT-IR spectroscopy of adsorbed carbon monoxide [S1]. FT-IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer within the spectral range of 700–6000 cm⁻¹.

Carbon monoxide is often used as a suitable probe molecule to study acidity of zeolites and zeolite-containing composites. Due to H-bonding with Brønsted acid sites (BAS), CO induces a broadening and a red-frequency shift of the bands of O-H groups. The higher acid strength of OH groups, the larger the shift of the OH modes.

Upon low temperature CO adsorption on ZSM-5(x)-Al₂O₃ composites, the band at 3612 cm⁻¹ (Figure SI-2) fully disappears, and the new band at 3280–3300 cm⁻¹ appears (Figure SI-3). The CO-induced shift of $\Delta\nu_{\text{O-H...CO}} = 332\text{--}312\text{ cm}^{-1}$ is typical value for ZSM-5 zeolites and corresponds to strongly acidic Brønsted sites. Other band in the O-H stretching region after CO adsorption on the composite samples detects at ~3430–3475 cm⁻¹ (Figure SI-3). This band is due to the shift of the bands at 3665 and 3740 cm⁻¹ (Figure SI-2) related to the extraframework Brønsted acid sites of zeolites: bridged Al-O(H)-Al and defective silanol OH groups (Si-OH...Al³⁺). The shift value ($\Delta\nu_{\text{O-H...CO}}$) is 235–265 cm⁻¹ and corresponds to moderately strong BAS, which are somewhat less acidic than the Si-O(H)-Al bridging groups in the zeolite channels.

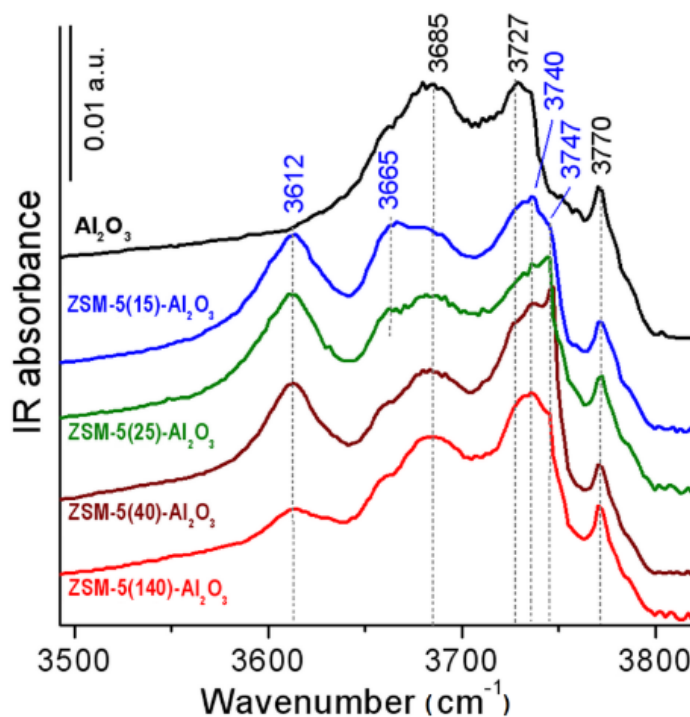


Fig. SI-3. FTIR spectra of Al₂O₃ and ZSM-5(x)-Al₂O₃ composites after outgassing at 500 °C in the O-H stretching region.

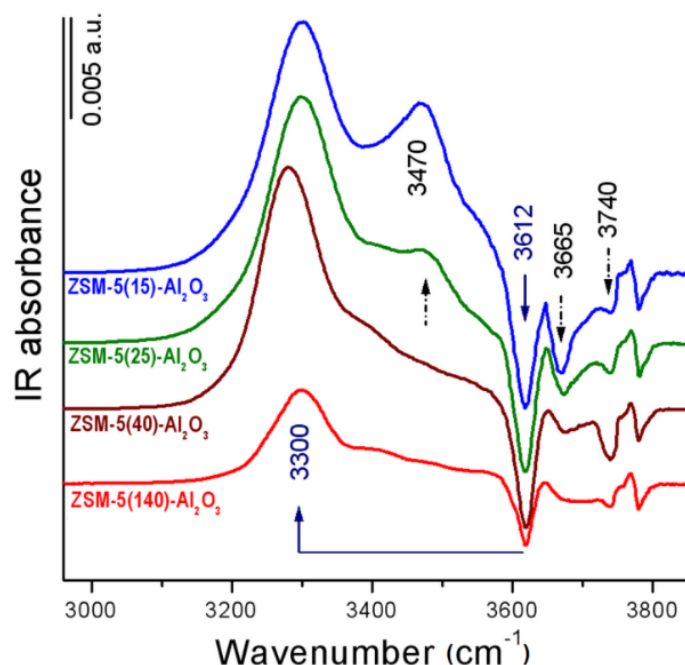


Fig. SI-4. IR difference spectra in the OH-region after CO adsorption at liquid nitrogen temperature and at equilibrium CO pressure of 1 mbar on ZSM-5(x)-Al₂O₃ composites.

According to the FT-IR data, the total concentration of strong BAS decreases in the following order: ZSM-5(15)-Al₂O₃ > ZSM-5(25)-Al₂O₃ > ZSM-5(40)-Al₂O₃ >> ZSM-5(140)-Al₂O₃ (Table SI-2).

Table SI-2. Type and concentration of Brønsted acid sites of ZSM-5(x)-Al₂O₃ composites [S1].

Type of sites	Absorbance bands, cm ⁻¹	Si/Al			
		15	25	40	140
Strong BAS in ZSM-5 channel, μmol g ⁻¹	VO-H...CO 3280–3300	28.8	27.0	24.6	8.1
Extraframework BAS in ZSM-5 zeolite, μmol g ⁻¹	VO-H...CO 3430–3475	27.9	17.3	8.4	1.8
Total BAS, μmol g ⁻¹		56.7	44.3	33.0	9.9

REFERENCES

[S1] Nuzhdin, A.L., Wang, Y., Vlasova, E.N., Bukhtiyarova, M.V., Danilova, I.G., Yashnik, S.A., Pochtar, A.A., Xiao, L., Wu, W., Bukhtiyarova, G.A., *Fuel*, 2024, vol. 356, p. 129622. <https://doi.org/10.1016/j.fuel.2023.129622>.