Electronic Supplementary Information for

Modified zeolite ZSM-5 for the methanol to aromatics reaction

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Methods:

Preparation and testing of Ga/ZSM-5 and Zn/ZSM-5

The catalysts were prepared *via* impregnation like in the case of Ag, Ni, Cu, Pd, Ir and Ru catalysts but using $Ga(NO_3)_3 \cdot xH_2O$ (Aldrich, assay 27%) and $Zn(NO_3)_2 \cdot 6H_2O$ (Aldrich, assay 24%) precursors. In order to obtain catalysts with a final metal loading of 1% wt, the desired amount of metal precursor was dissolved in water (25 mL) and mixed with zeolite ZSM-5 (ca. 2 g) under vigorous stirring. The amount of zeolite was adjusted to compensate the metal assay for each precursor. The resulting slurry was heated up slowly to 80 ^oC and evaporated to dryness. Each catalyst was dried at 120 ^oC for 16 h, and calcined at 550 ^oC for 4 h in static air (temperature ramp 20 ^oC min^{-1}). The catalytic tests were performed in identical manner to that reported for the other metals in the main body of the manuscript.

Unit cell parameters determination

Unit cell parameters were determined using Rietveld refinement[1] as full-pattern fit algorithm for catalyst, and the goodness of fit between experimental and simulated XRPD spectra was evaluated *via* χ^2-test.[2] Initial atomic coordinates values to perform the fitting were obtained using crystallographic information files (CIF) available at the Database of Zeolite Structures (IZA-SC).[3]

Reduction and testing of Ag/ZSM-5 catalyst

The Ag/ZSM-5 catalyst obtained *via* impregnation was reduced under a low of 10 mL min^{-1} of a 5% H_2 in N_2 mixture, at 550 ^oC for 4 h. The resulting reduced catalyst was tested in an identical manner than the non reduced material.

Catalytic tests of propene, propane and butane over ZSM-5

Catalytic tests for the hydrocarbon aromatisation reactions over ZSM-5 were carryed out by mixing the hydrocarbons in a current of N_2, with a final flow of 88 mL/min using a volume fraction of 1% for propene and propane, and 2% for *n*-butane. All the other reaction conditions were the same as for the methanol tests, i.e. : all the catalysts were prepared in pellets form, obtained by pressing the solids at 2 tons $\cdot$ cm^{-2} for 1 min twice. The pellets were then ground and sieved, collecting the fraction between 850 and 600 μm. The reaction were carried out using a glass reactor at 450 ^oC under N_2 flow (88 mL min^{-1}, inlet pressure 4.5 bar).

Tables and Figures:

Table S1: Representative, detailed, product distribution in the MTA reaction for ZSM-5, Ir/ZSM-5, Ru/ZSM-5, Pd/ZSM-5, Ag/ZSM-5, Cu/ZSM-5, Ni/ZSM-5 (the metal loading for all catalysts was 1% wt).

Products	ZSM-5	Ir/ZSM-5	Ru/ZSM-5	Pd/ZSM-5	Ag/ZSM-5	Cu/ZSM-5	Ni/ZSM-5
Methane	1.8	1.2	1.1	2.3	2.1	2.5	11.6
Ethylene	15.8	14.5	14.4	16.6	11.2	8.9	8.9
Ethane	0	1.5	1.5	1.8	1.2	1.0	1.8
Propene	22.1	22.4	22.6	21.7	16.0	11.3	7.5
Propane	5.7	3.1	2.7	2.6	2.0	2.9	1.8
Dimethyl ether (DME)	0	0	0	0	0	0	0
Isobutane	13.6	12.2	12.0	8.5	8.6	9.6	6.3
Isobutene	0	0	0	0	0	0	0
1-butane	3.6	7.2	7.1	5.7	4.9	0	0
Butane	3.2	1.5	1.5	1.2	1.0	3.9	2.3
Pentane	0	0.9	0.9	0.7	0.7	0.9	0.6
Hexane	0.4	0.5	0.5	0.3	0.4	0.5	0.3
Benzene	1.6	1.5	1.5	1.8	2.7	2.3	2.8
Toluene	6.7	6.0	6.1	7.6	10.2	7.4	8.1
Ethylbenzene	0	0	0	0	0	0	0.2
p-xylene	9.0	9.2	9.2	10.4	13.6	10.3	14.3
o-xylene	2.7	2.7	2.7	3.1	4.0	3.2	4.2
Ethylmethylbenzene	3.9	4.0	4.1	5.4	8.1	8.1	9.3
Trimethylbenzene	0.9	1.0	0.9	1.2	1.6	1.6	1.1
Tetramethylbenzene	0	0	0	0	0.4	1.4	0.7
Naphthalene	0	0	0	0	0	0	7.5
Pentamethylbenzene	0	0	0	0	0	0	0
2-butenes	1.6	0	0.7	0	0	0.7	0.9
Pentenes	4.8	6.5	6.3	4.5	4.9	5.6	4.7
Hexenes	0	0	0	0	0	0	0
eptanes/eptenes	0	0	0	0	0	0	0
octanes/octanes	1.7	3.2	2.3	2.7	3.5	3.2	1.8
C_9 aromatics	0.9	0.9	1.9	1.9	2.9	5.1	2.9
C_{10} aromatics	0	0	0	0	0	2.9	0.4
C_{11} aromatics	0	0	0	0	0	6.7	0
C_{11+} aromatics	0	0	0	0	0	0	0

The chromatographic method used, allowed to resolve 22 products (pale blue lines) and to identify class of products per groups (yellow lines)

In this table, with respect to the notation used in the main body of the manuscript, and the resolution capability of our chromatographic method, the grouping is the following:

C_4-C_5 isomers: C_4 are the 2-butene (*cis* and *trans*) and C_5 are pentenes derivatives (1-, 2- and the corresponding *cis* and *trans* forms).
C_6-C_8 isomers: comprises: hexene isomers, epatanes/eptenes, octanes/octanes with all their possible combinations of double bond in different position, cis and trans form and branched alkanes.
C_9-C_{11+} isomers: include branched and unsaturated aromatics products either with alkyl chain or unsaturated branched substituents.

The grouping was carried out in order to highlight the most relevant products in the MTA reaction.

Table S2: Carbon mass balance per time on stream in the MTA reaction for ZSM-5, Ir/ZSM-5, Ru/ZSM-5, Pd/ZSM-5, Ag/ZSM-5, Cu/ZSM-5, Ni/ZSM-5 (the metal loading fro all metals was 1% wt).

time (min)	ZSM-5	Ir/ZSM-5	Ru/ZSM-5	Pd/ZSM-5	Ag/ZSM-5	Cu/ZSM-5	Ni/ZSM-5
53	99.5	99.2	99.6	99.2	99.3	99.8	99.6
106	99.1	98.2	99.8	98.2	99.8	99.3	99.5
159	99.8	99.5	100.0	99.5	99.4	99.1	99.3
212	99.2	99.8	99.5	99.8	99.6	99.5	99.9
265	99.5	99.2	99.7	99.2	99.8	99.6	100.0
318	99.5	99.7	100.0	99.7	99.2	99.9	100.0
371	100.0	99.9	99.3	99.9	99.8	99.4	99.6
424	99.3	100.0	99.5	100.0	99.9	99.2	99.2
477	99.3	99.4	99.5	99.4	99.4	99.5	99.5
530	99.7	99.6	99.8	99.6	100.0	99.6	99.4
583	99.2	99.2	99.4	99.2	99.5	99.8	99.6
636	99.5	99.8	99.8	99.8	99.7	99.4	99.7

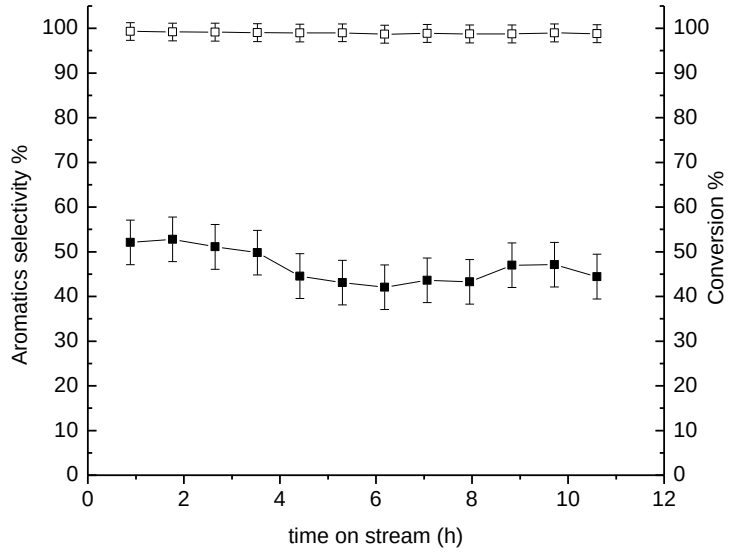

Figure S1: (■) conversion and (□) selectivity to aromatics in the reaction of methanol over 1% wt Ga/ZSM-5 catalyst.

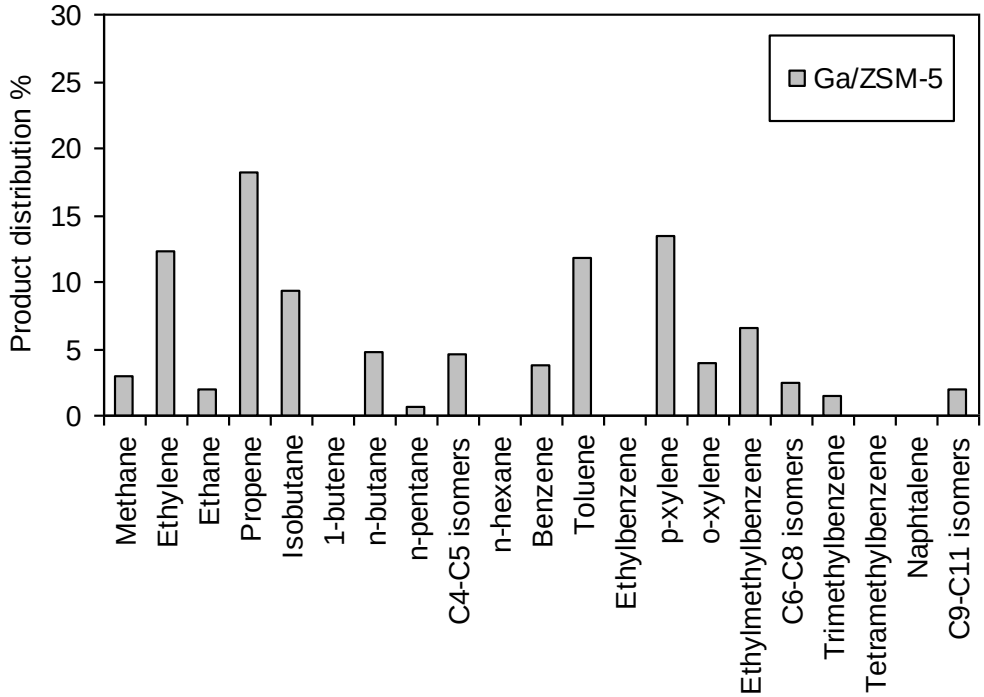

Figure S2: Product distribution for 1% wt Ga/ZSM-5 catalyst in the MTA reaction. (C_9-C_{11} isomers: aromatic products).

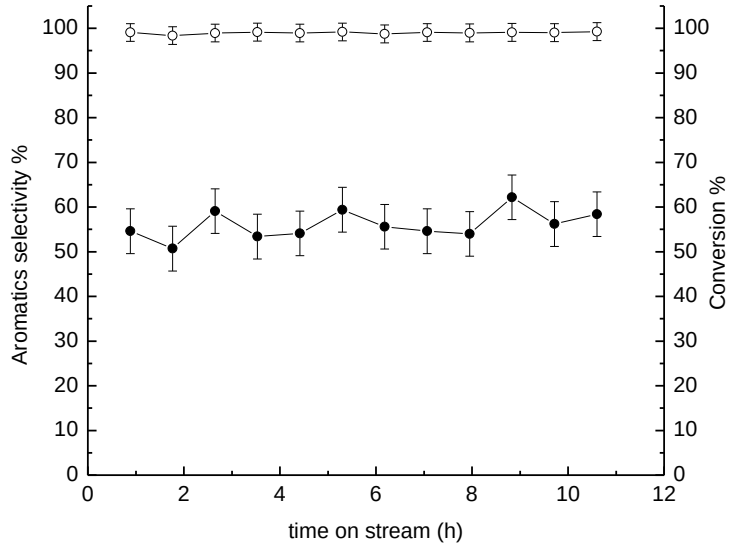

Figure S3: (●) conversion and (○) selectivity to aromatics in the reaction of methanol over 1% wt Zn/ZSM-5 catalyst.

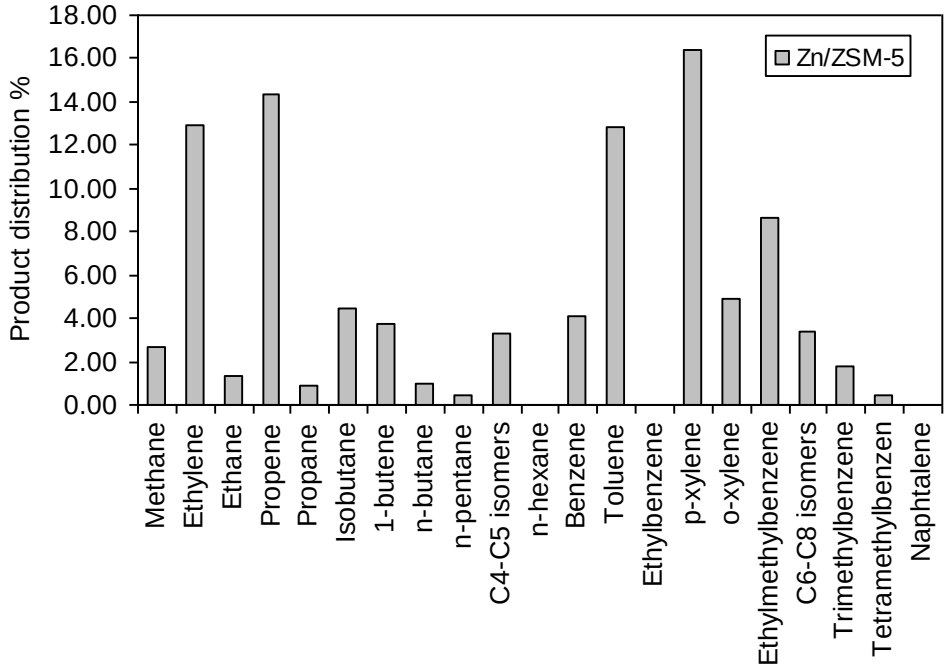

Figure S4: Product distribution for 1% wt Zn/ZSM-5 catalyst in the MTA reaction. (C_9-C_{11} isomers: aromatic products).

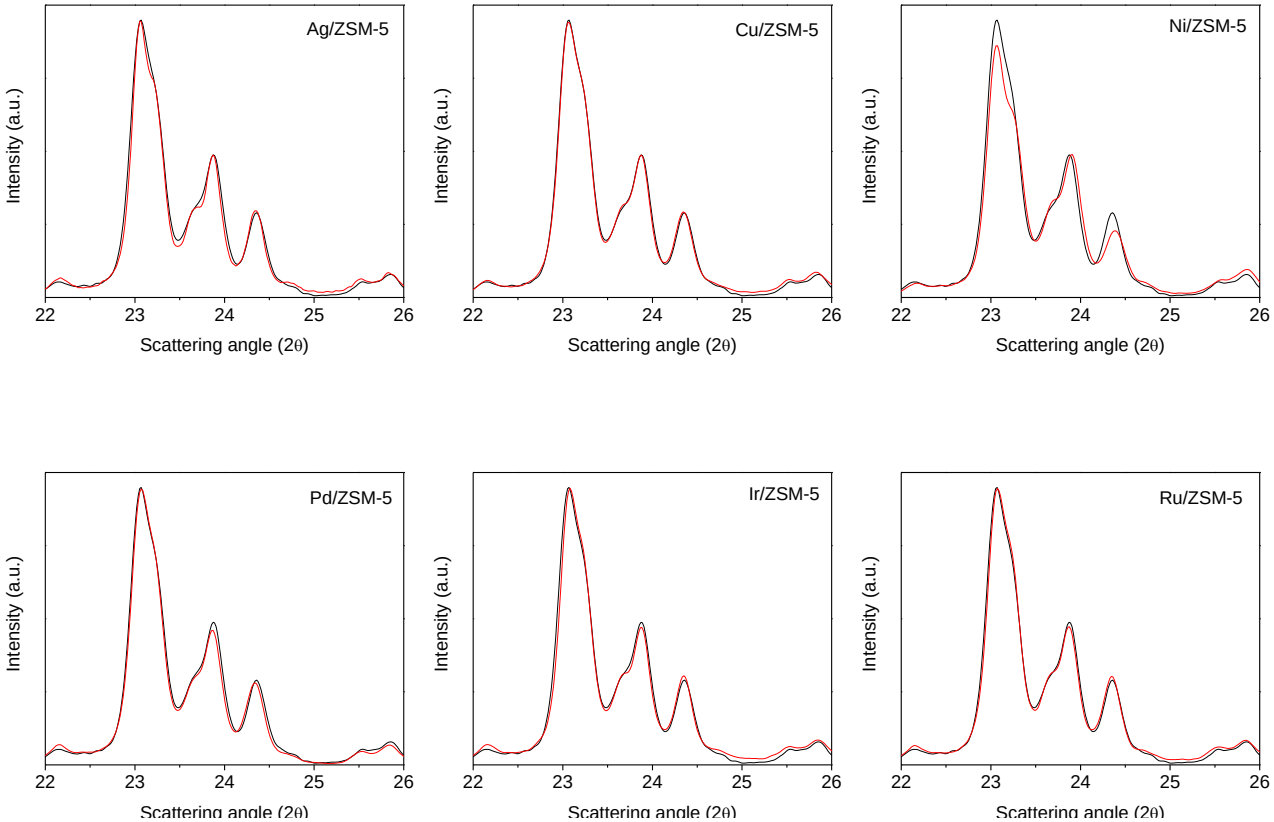

Figure S5: Enlarged 2θ region from 22 to 26° for the aluminium framework of Ag/ZSM-5, Cu/ZSM-5 and Ni/ZSM-5 (red line, top XRPD patterns) and Pd/ZSM-5, Ir/ZSM-5 and Ru/ZSM-5 (red line, bottom XRPD patterns). ZSM-5 (black line) is reported in all patterns for comparison.

No significant difference in present among the samples but a slight distortion for Ni/ZSM-5.

Table S3: unit cell parameters for ZSM-5, Pd/ZSM-5, Ir/ZSM-5, Ru/ZSM-5, Ag/ZSM-5, Ni/ZSM-5 and Cu/ZSM-5 (the metal loading for all catalysts was 1% wt).

Sample	Structural parameters (Å)			V (Å)^3
	a	*b*	*c*	
ZSM-5	20.105	19.944	13.415	5379
Pd/ZSM-5	20.109	19.900	13.411	5367
Ir/ZSM-5	20.101	19.955	13.427	5386
Ru/ZSM-5	20.101	19.956	13.424	5385
Ag/ZSM-5	20.098	19.949	13.420	5381
Ni/ZSM-5	20.184	19.960	13.440	5415
Cu/ZSM-5	20.142	19.972	13.446	5409

It should be noted that the fitting procedure was carried out on an orthorhombic unit cell ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90^o$) rather than a monoclinic unit cell ($a \neq b \neq c$, $\alpha \neq 90^o$ $\beta = \gamma = 90^o$).[4] This is consisted with calcined ZSM-5 samples and with a SiO_2:Al_2O_3 ratio less than 160. [5,6]

Only a slight increase in the unit cell volume (*ca.* 0.6%) was detected for the Ni/ZSM-5 sample.

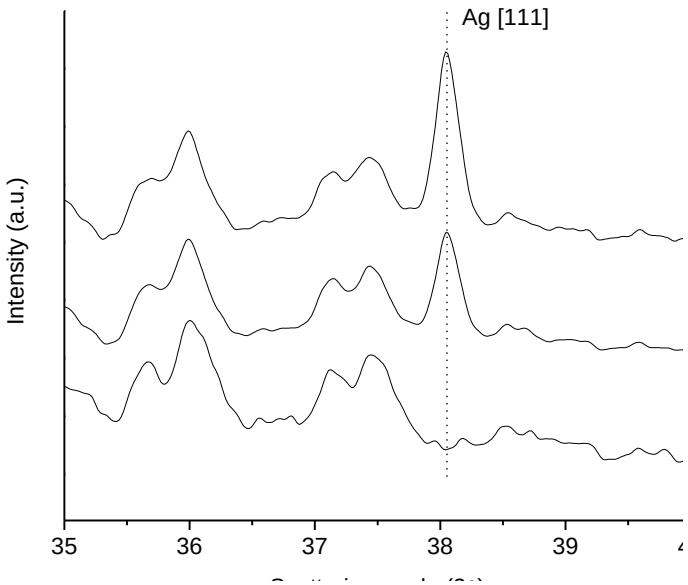

Figure S6: Reduction and formation of Ag metal in the MTA reaction (highlighted by the Ag[111] reflection) from a 1% wt Ag/ZSM-5 for: (a) fresh catalyst, (b) catalyst after 5.5 h time on stream and (c) catalyst after 11 h time on stream.

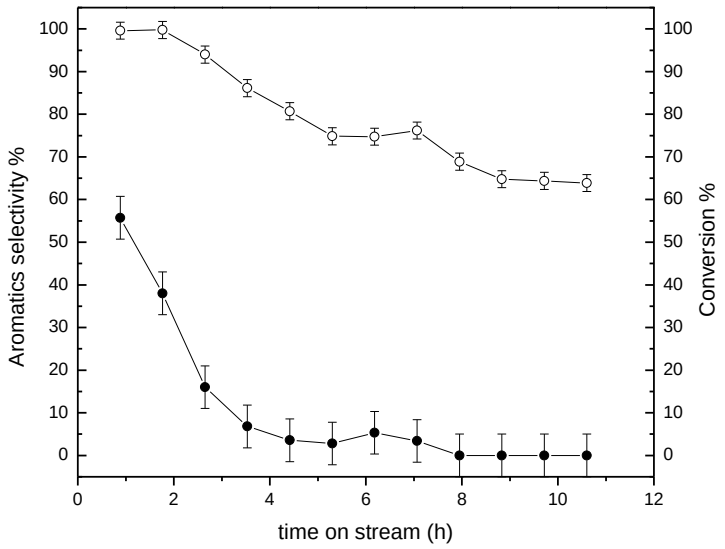

Figure S7: (●) conversion and (○) selectivity to aromatics in the reaction of methanol in a fully reduced 1% wt Ag/ZSM-5 catalyst pre-treated with H_2 for 4h at 550 ^{o}C.

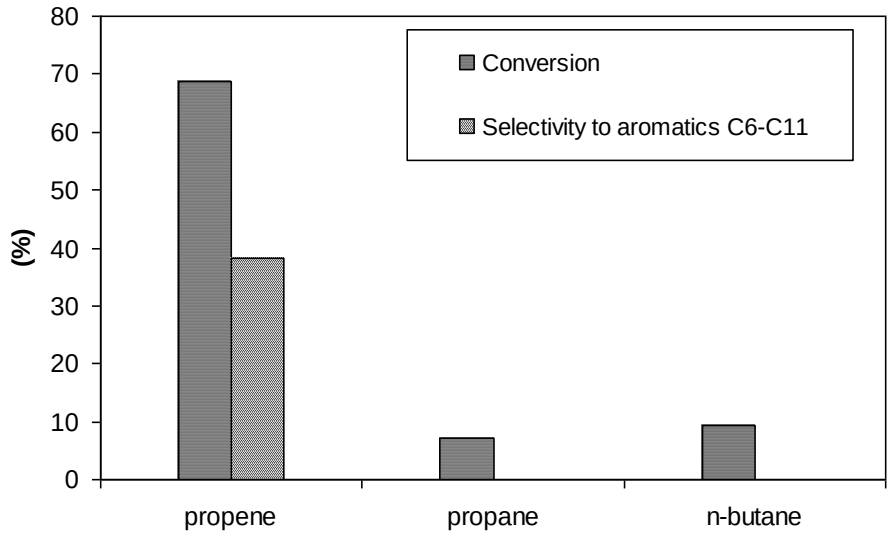

Figure S8: Conversion and selectivity to aromatics obtained feeding of ZSM-5 with propene, propane and *n*-butane.
Aromatics can be detected only using propene as substrate.

References

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