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(54) **SOLID PHOSPHORIC ACID CATALYST, AND METHOD FOR PRODUCING TRIOXANE**

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(56) **References Cited**

U.S. PATENT DOCUMENTS

5,508,448	A	4/1996	Emig et al.
6,124,480	A	9/2000	Hoffmockel et al.
6,313,323	B1	11/2001	Werner et al.

FOREIGN PATENT DOCUMENTS

CA	771679	A	11/1967
EP	0714379	B1	10/1997
JP	S44-12898		6/1965
JP	S44-30735		12/1969
JP	S59-25387		2/1984
JP	S59-134789		8/1984
JP	H7-2833		1/1995
JP	2001-11069		1/2001
JP	2005-230622		9/2005
JP	2014-024754		2/2014
WO	WO2014/017203		1/2014

OTHER PUBLICATIONS

Busfield, et al.; "The Gas-phase Equilibrium between Trioxan and Formaldehyde: The Standard Enthalpy and Entropy of the Trimerisation of Formaldehyde" J. Chem. Soc. (A), 1969 pp. 2975-2977.

Suprun et al, Acidic catalysts for the dehydration of glycerol: Activity and deactivation, Journal of Molecular Catalysis A: Chemical, Elsevier, Amsterdam, NL, vol. 309, No. 1-2, Aug. 18, 2009, pp. 71-78.

Extended European search report in European Patent Application No. 14797038.8 dated May 25, 2016.

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(57) **ABSTRACT**

A solid phosphoric acid catalyst which, when gas-phase synthesizing trioxane from formaldehyde, results in production of trioxane at a high yield and at a high selection rate by markedly suppressing side reactions, reduces the adhesion of organic matter to the catalyst surface, and achieves a stable and long-term catalyst reaction. This solid phosphoric acid catalyst contains silicon phosphate oxide (SPO) obtained by sintering at a temperature of at least 200° C. a carrier material to which a phosphoric acid component has been added, and the total quantity of acid does not exceed 5 mmol per 1 g of solid phosphoric acid catalyst when calculated as acid quantity determined by NH_3-TPD measurement.

8 Claims, 1 Drawing Sheet