An integrated process for partial oxidation of alkanes

Xiao-Ping Zhou,[a] **Aysen Yilmaz,**[a] **Gurkan A. Yilmaz,**[a] **Ivan M. Lorkovic,**[a] **Leroy E. Laverman,**[a]
Michael Weiss,[b] **Jeffrey H. Sherman,**[b] **Eric W. McFarland,**[*bc] **Galen D. Stucky**[*a] **and Peter C. Ford**[*a]

[a] *Department of Chemistry and Biochemistry, University of California, Santa Barbara, California, USA.
E-mail: GDS; stucky@chem.ucsb.edu, EWM; mcfar@engineering.ucsb.edu, PCF; ford@chem.ucsb.edu;
Fax: +1 805-893-4120*
[b] *GRT, Inc, 5662 Calle Real #373, Santa Barbara, CA 93106, USA*
[c] *Department of Chemical Engineering, University of California, Santa Barbara, California, USA*

**The partial oxidation of alkanes *via* bromination followed by
the reaction with solid metal oxide mixtures (MO) is shown
to give an array of products that can be tuned by varying the
MO and the reaction conditions.**

The transformation of natural gas feedstocks to higher value
compounds continues to present an important challenge with
strong economic rationales.[1] For example, > 42 million metric
tons of ethylene were produced in the U.S. and western Europe
in 2001,[2] and improvements in the efficiencies of alcohol or
alkene production from alkane precursors could have an
enormous impact. Here we describe an integrated, multi-step
process for the selective partial oxidation of alkanes to alcohols,
ethers or alkenes that provides unprecedented product con-
trol.[3]

These transformations are carried out in a sequential zone
flow reactor (SZFR) and are illustrated in Scheme 1 for the
partial oxidation of ethane. The first step is the bromination of
alkane to alkyl bromide(s) and HBr. This mixture is then
allowed to react with a supported metal oxide (MO) to
neutralize the HBr and to generate oxygenated products or
alkenes (depending upon the conditions) plus solid metal
bromide. Lastly, oxygenation of the spent solid regenerates the
MO and Br_2 for reuse. Thus, the overall transformation of
alkane to alcohol, ether, or alkene utilizes dioxygen as the
ultimate oxidant, for example:

$$R–H + \tfrac{1}{2} O_2 \rightarrow ROH \qquad (1)$$
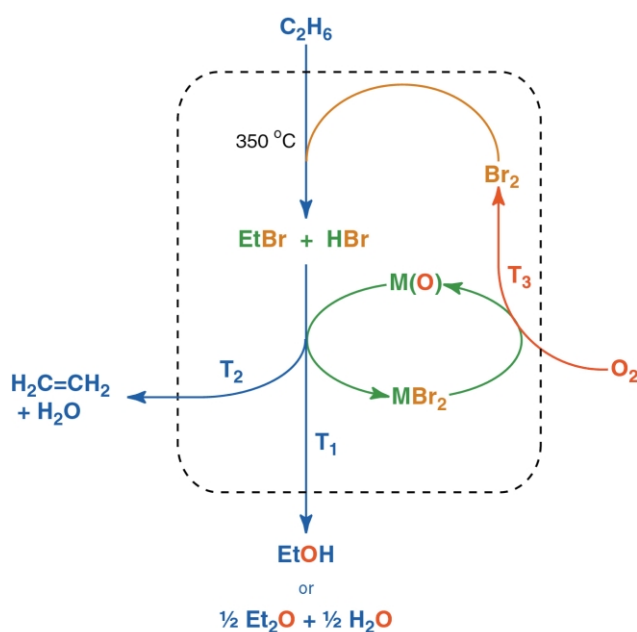

Scheme 1

The key to this process is the use of a solid transition metal
oxide or MO mixture on a stable support to react with the alkyl
bromide and to effect bromide/oxide metathesis under mild
conditions. While others have considered related approaches,[4]
the integration of these steps described here is unique.
Furthermore, we have demonstrated that the specific MO
composition and reaction conditions determine product dis-
tribution. For example, with ethane, certain MO compositions
give mostly ethanol, while others give predominantly diethyl
ether. Further changes in the conditions tune the reaction to give
ethylene as the maximized product. Thus, a major advantage of
the systems described here is that it provides a flexible platform
with remarkable product tunability.

The SZFR consists of two serial fixed bed reactors with
independent temperature control. In the first, a stream of Br_2
and excess alkane (1–3 bar) reacts over glass beads (60–120
mesh) at 350 °C and the Br_2 is fully consumed. The resulting
alkyl bromide(s), HBr and excess alkane are directed into a
second reactor containing supported metal oxide at T_1 or T_2
(200–350 °C). The exiting products were identified and
analyzed by ^{1}H-NMR and GC (with MS, TCD or FID detection)
techniques. Longer runs demonstrate that most of the oxide
equivalents of MO can be utilized. After the oxide capacity is
expended, O_2 is passed into the second reactor at T_3 (300–500
°C depending on the nature of the metathesis reactant) to
regenerate MO and Br_2. When the MO mixtures included redox
active transition metals, bromide retained on the spent solid was
quantitatively recovered as Br_2. Repetitive runs (> 25 cycles)
with regenerated MO showed no loss of activity. Material
balances were established for bromine and carbon.

Although developing a selective catalysis for alkane bromi-
nation remains a challenge, monobromination can be achieved
noncatalytically using excess alkane. With a 10.5 : 1 alkane to
Br_2 ratio the monobromination selectivity for ethane is 94%
with 9% conversion. The other products are largely dibromo-
ethane.

Representative solid reactants for oxide : bromide metathesis
are 50 : 50 CuO : ZrO_2 (MO-1) and 43 : 7 : 50 Co_3O_4 : Sm_2O_3
: ZrO_2 (MO-2) and 50 : 50 Co_3O_4 : ZrO_2 (MO-3). Products from
MO-1 and MO-2 differ considerably. At lower temperatures
(200–250 °C) MO-1 gives predominantly alcohols and more
deep-oxidation to CO_2, while MO-2 gives largely ethers. The
relative yields are very sensitive to MO composition and
reaction conditions. For example, with ethane, ethanol and
diethyl ether are the principal products for MO-1 and MO-2
respectively operating at 200–250 °C. Lesser products include
ethylene, acetaldehyde, vinyl bromide, ethyl acetate and
butadiene, and unreacted EtBr.† Although not described here,
certain variations of the MO compositions and temperatures
have been demonstrated to increase the selectivities toward one
or another of these lesser products.

The product sensitivity to MO composition and conditions is
illustrated by the three systems summarized in Fig. 1. For
example, reaction of the bromoethanes formed from a 10.5 : 1
C_2H_6 : Br_2 stream with MO-2 (5 g) at 200 °C gave about 15%
ethanol and 50% diethyl ether (based on the converted
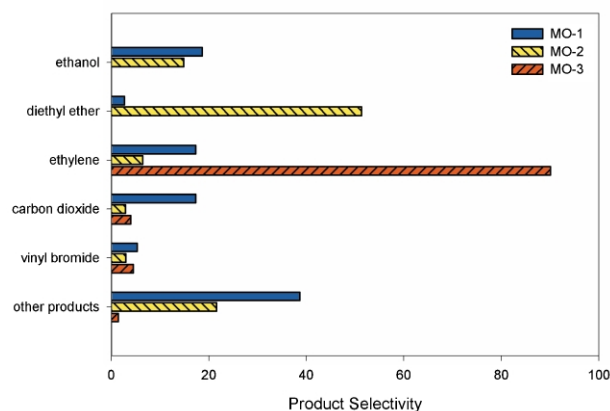
Fig. 1 Product selectivity using an ethane : bromine feed reacting with three MO compositions. The reaction conditions were as follows: MO-1 (5 g, 250 °C, C_2H_6 : Br_2 = 8 : 1); MO-2 (5 g, 200 °C, C_2H_6 : Br_2 = 10.5 : 1) and MO-3 (2 g, 350 °C, C_2H_6 : Br_2 = 10.5 : 1). The yields reported were normalized to account for unreacted EtBr.

bromoalkane). For both MO-1 and MO-2 ethylene was also formed and higher *T* favored this product. In this context, Fig. 2 illustrates a SZFR study using a 10.5 : 1 C_2H_6 : Br_2 stream using MO-3 in the second reactor at 350 °C. The product selectivity toward ethylene was more than 80% with much of the remainder being EtBr, which can be recycled. (When pure EtBr was used as a feedstock under analogous conditions, the product selectivity toward ethylene was 95%.)

Efficient and selective methane activation remains a chemical "holy grail" and has been the subject of numerous elegant studies.[5] With our system, the conversion of methane to MeOH
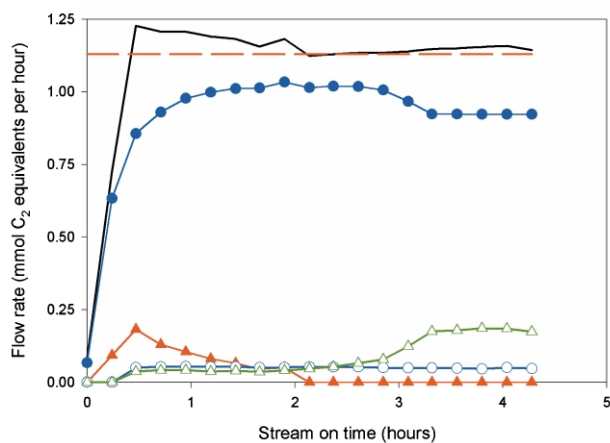
Fig. 2 Temporal output for ethane partial oxidation in a SFZR run using MO-3 at 350 °C and an ethane : bromine feed (10.5 : 1). solid circles = ethylene, solid triangles = CO_2, open triangles = ethyl bromide, open circles = all other products, solid line = carbon mass balance, dashed line = carbon input.

or Me_2O is readily accomplished but selectivity remains an issue, largely because of the lower bromination selectivity. Reaction of the bromomethanes formed from a 10 : 1 CH_4 : Br_2 stream with MO-1 at 250 °C gave CH_3OH (52% based on the converted bromoalkane) but a large amount of CO_2 (48%), while the same feed into the MO-2 gave CH_3OH (44%), $(CH_3)_2O$ (44%) and CO_2 (11%). Thus, these systems offer promise for methane activation as well.

In summary we have described a new approach toward the selective partial oxidation of alkanes using oxygen as the ultimate oxidant. Of particular note is the use of solid metal oxides to effect the conversion of alkyl bromide intermediates to alcohols or ethers or to alkenes. By varying the specific MO compositions and conditions, this system provides unprecedented product control as illustrated by the three examples shown in Fig. 1. Ongoing studies are focused on improving overall conversion and controlling product selectivity and include investigations of bromination catalysis and the design and optimization of metathesis solids and conditions.

Notes and references

† Reactions were run under conditions where there was incomplete (50–80%) conversion of EtBr to evaluate effects of systematic changes on activities. Although unreacted EtBr would be consumed by using longer space times or by recycling through the metathesis reactor, under these conditions the total conversion of ethane to products other than bromo-carbons was 5–7% in a single pass. Reactions of pure EtBr with various MO give product distributions very similar to those found for the stream from the bromination reactor with the notable absence of vinyl bromide. The latter is apparently the result of the modest polybromination occurring during the first step.

1 H. Arakawa, M. Aresta and J. N. Armor *et al.*, *Chem. Rev.*, 2001, **101**, 953.
2 *Chem. Eng. News.*, 2002, **80**, 42.
3 X. P. Zhou, I. Lorkovic and J. H. Sherman, (GRT, Inc.) Integrated process for synthesizing alcohols, ethers, and olefins from alkanes. US. Patent 6,486,368, November 6, 2002.
4 *e.g.* (*a*) R. W. King, *Hydrocarbon Processing*, 1966, **45**, 189; (*b*) G. Lester (Universal Oil Products, USA). Bromine Recovery U.S. Patent 3,310,380, March 21, 1967; (*c*) W. J. Pieters, E. J. Carlson, W. E. Gates and W. C. Conner, (Allied Chemical Corp., USA). Pyrogenic silica or titania or alpha-alumina cuprous chloride catalyst of hydrogen chloride/oxygen reaction. U.S. Patent 4,123,389, February 2, 1977; (*d*) G. A. Olah and B. Gupta et al, *J. Am. Chem.. Soc.*, 1985, **107**, 7097; (*e*) K. Viswanathan, , H. C. B. Chen and , S. W. Benson, (Occidental Chemical Corp., USA). Production of ethylene or a mixture of ethylene and vinyl chloride. European Patent WO9210447, June 25, 1992; (*f*) M. Mortensen, R. G. Minet, T. T. T. Storsis and S. Benson, *Chem. Eng. Science*, 1996, **51**, 2031–2039; (*g*) I. V. Mishakov and K. J. Klabunde *et al.*, *J. Catalysis*, 2002, **206**, 40.
5 *e.g.* (*a*) B. A. Arndtsen, R. G. Bergman, T. A. Mobley and T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154; (*b*) R. A. Periana and D. J. Taube et al., *Science*, 1998, **280**, 560; (*c*) S. Mukhopadhyay and A. T. Bell, *Angew. Chem. Int. Ed.*, 2003, **42**, 1019.