RSC Advances



View Article Online

View Journal | View Issue

PAPER



Cite this: RSC Adv., 2016, 6, 114123

Partial oxidation of 2-methyl-1,3-propanediol to methacrylic acid: experimental and neural network modeling

Mohammad Jaber Darabi Mahboub,^a Mohammad Rostamizadeh,^b Jean-luc Dubois^c and Gregory S. Patience^{*a}

Methacrylic acid (MAA) is a specialty intermediate to produce methyl methacrylate (MMA), which is a monomer for poly methyl methacrylate. Current processes to MMA and MAA rely on expensive feedstocks and multistep processes. Here we investigate the gas-phase oxidation of 2-methyl-1,3-propanediol (2MPDO) to MAA over heteropolycompounds as effective catalysts, finding that the maximum selectivity to MAA was 41% with 63% conversion of reactant at 250 °C over Cs(NH₄)₂PMo₁₂O₄₀(VO)Cu_{0.5}. Cesium (Cs) stabilized the catalyst structure at 250 °C, and vanadium(v) and copper (Cu) played a positive role as an oxidant and promoter, respectively. A 0.3 mm nozzle atomized the liquid reactant over the catalyst surface into a μ fluidized bed reactor. The proposed Artificial Neural Network (ANN) model predicts MAA selectivity based on 2MPDO and oxygen compositions and catalyst components (Cs, V, Cu) as independent factors. The model accounts for 97% of the variance in the data ($R^2 = 0.97$). Vanadium as a catalyst component and oxygen concentration are the two most significant factors. Genetic algorithms (GA) coupled with ANN modeling optimized the input parameters to improve the selectivity. The selectivity to MAA over the optimized catalyst (Cs(NH₄)₂PMo₁₂O₄₀(VO)Cu_{0.15}) and optimum feed compositions (2MPDO/O₂/Ar = 13%/ 10%/77%) was 43% at 250 °C.

Received 27th June 2016 Accepted 22nd November 2016 DOI: 10.1039/c6ra16605a

www.rsc.org/advances

1 Introduction

Methyl methacrylate (MMA) is a constituent in paint, coating dispersion agents, modifiers for PVC, bone inserts and is a monomer for poly-methyl-methacrylate (PMMA).¹⁻⁵ One process to produce MMA is based on acetone and cyanohydrin but the reactants are expensive and it generates a high volume of byproducts.6-10 Methacrylic acid (MAA) is the principal monomer to produce poly(methacrylic acid); however, it is a potentially economic feedstock to produce methyl methacrylate. Catalyst lifespan, multi-step reaction processes and low conversion impede the commercialization of the oxidation of light hydrocarbons (ethylene, propylene, isobutene and isobutane) to MAA.^{1,6,11-23} Recently, we proposed the gas-phase partial oxidation of 2-methyl-1,3-propanediol (2MPDO) to MAA and methacrolein (MAC) rather than olefins. After 1 h time-onstream, MAA selectivity in the fluidized bed reactor reached 41%.24,25

Reaction conditions and catalyst composition are the main factors to maximize MAA selectivity. Many studies compare the performance of metals versus non-metal ions in the catalyst. Keggin-type polyoxometalates containing phosphorus and molybdenum are the most active and selective heterogeneous catalysts for the oxidation of isobutane and 2MPDO to MAA.^{1,12,15-26} However, phosphomolybdic acid $(H_3PMo_{12}O_{40})$ is a poor and non-stable catalyst to oxidize lower alkanes,²⁷ though inserting metal ions and protons into the catalyst structure enhanced catalyst performance.28-30 Substituting Cs+ with H+ in H₃PMo₁₂O₄₀ enhances MAA + MAC yield.^{16,25,28} Cesium forms an alkaline salt in the catalyst structure and acts as a support over which the active phase is dispersed and thermally stabilized.^{6,18,21,22,25,29} Ammonium ions increase the surface area and enhance MAA selectivity.^{16,17,31,32} Vanadium in the form of V⁵⁺ reduces Mo⁶⁺ to Mo⁵⁺, which improves or accelerates both the reduction and reoxidation steps and consequently increases catalytic activity.^{22,31-34} Copper (Cu) acts as a promoter into the catalyst structure.23,25 Partially substituting iron in a Keggin anion decreases selectivity to MAA and conversion.¹⁰ However, it increases selectivity by inserting into the catalyst structure as a counter cation.^{10,35,36} Langpape *et al.* demonstrated that inserting iron into the acid structure of the support on the cesium salt increases selectivity without changing the activity of the acid phase.³⁷ Tellurium as Te⁴⁺ is a counter-cation that

^aChemical Engineering Department, École Polytechnique de Montréal, 2900 Boul. Édourd-Montpetit, Montréal, Canada. E-mail: gregory-s.patience@polymtl.ca; Fax: +1 514 340 4059; Tel: +1 514 340 4711

^bChemical Engineering Department, Sahand University of Technology, Sahand New Town, P.O. Box: 51335-1996, Tabriz, East Azerbaijan, Iran

ARKEMA, 420 Rue d'Estienne d'Orves, 92705 Colombes, France

Table 1 Summary of MAA and MAC production over different kinds of catalysts

				Selectivity		
Used catalyst	inert/water	Conversion (%)	Temp. (°C)	MAA	MAC	Ref.
$H_3PMo_{12}O_{40}$	26/13/49/12	4	340	4	12	16
$H_4PMo_{11}O_{40}$	26/13/49/12	3	340	25	39	16
Cs _{1.15} (NH ₄) _{1.85} HPMo ₁₁ VO ₄₀	26/13/49/12	6	340	45	15	16
$(NH_4)_3 PMO_{12}O_{40}$	26/13/49/12	4	340	33	21	16
$(NH_4)_3HPMO_{11}VO_{40}$	26/13/49/12	2	340	49	32	16
Cs _{2.5} H _{0.5} PMo ₁₂ O ₄₀	17/33/50/0	16	340	24	7	9
$Cs_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$	17/33/50/0	24	340	27	6	9
$Cs_{2.5}Ni_{0.08}H_{1.34}PVMo_{11}O_{40}$	17/33/50/0	31	340	29	4	6
$Cs_2HPMo_{12}O_{40}$	17/33/50/0	11	340	34	10	23
$Cs_2Te_{0.3}V_{0.1}H_xPMo_{12}O_{40}$	27/13.5/49.5/10	16	350	54	11	34
H _{1.8} Te _{0.6} PMo ₁₂ O ₄₀	27/13.5/49.5/10	6	355	27	22	34 and 38
$Cs_2Fe_{0.2}H_{0.4}PMo_{12}O_{40}$	33.4/17.2/49.4/0	7	340	24	17	37
Fe _{0.85} H _{0.45} PMo ₁₂ O ₄₀	33.4/17.2/49.4/0	4	340	9	27	37
Cs ₂ HPMo ₁₂ O ₄₀	33.4/17.2/49.4/0	7	340	12	14	37
Cs _{1.5} Fe _{0.5} (NH ₄) ₂ PMo ₁₂ O ₄₀	25/25/35/15	8	360	21	4	10
Cs _{1.5} (NH ₄) ₂ PMo _{11.5} Fe _{0.5} O _{39.5}	25/25/35/15	8	360	15	4	10
H _x Fe _{0.12} Mo ₁₁ VPAs _{0.3} Oy	29/29/42/0	24	370	70	4	7
Cs _{2.5} Fe _{0.08} H _{0.26} PMo ₁₂ O ₄₀	17/33/50/0	14	340	_	30	35
H ₄ PVMo/Cs ₃ PMo ₁₂ O ₄₀	26/13/49/12	5	340	42	17	21
Fe _{0.5} (NH ₄) _{2.5} PMo ₁₂ O ₄₀	26/13/49/12	6	350	32	14	36
$(NH_4)_3 PMo_{12}O_{40}$	26/13/49/12	7	380	40	11	17
$(NH_4)_3 PMO_{12}O_{40}/Sb_{0.23}O_x$	26/13/49/12	6	350	45	12	17
(NH ₄) ₃ HPMo ₁₁ VO ₄₀ /CPM ^a	27/13.5/49.5/10	15	340	42	10	32
(NH ₄) ₃ HPMo ₁₁ VO ₄₀ /SiO ₂	27/13.5/49.5/10	11	340	13	15	32
$(NH_4)_3HPMO_{11}VO_{40}$	27/13.5/49.5/10	3	340	34	20	32
40 wt% $(NH_4)_3HPMo_{11}VO_{40}$ and 60 wt% CPM ^{<i>a</i>}	27/13.5/49.5/10	15	340	42	10	17
(NH ₄) ₃ PMo ₁₂ O ₄₀ /silica	26/13/49/12	10	350	37	3	26
$Cs(NH_4)_2PMo_{12}O_{40}(VO)Cu_{0.5}$	13/10/77/0	63	250	41	33	25
^{<i>a</i>} CPM: Cs ₃ PMo ₁₂ O ₄₀						

enhances selectivity to MAA and MAC.^{34,38} Hundreds of catalysts oxidize isobutane MAA and MAC (Table 1).

Identifying the optimal catalyst composition that maximizes yield and selectivity is time consuming.39 Combinational methods and Design Of Experiments (DOE) reduce the number of experiments and identify better experimental strategies to establish the best combination of promoters and dopants.³⁹ Black box modeling and optimization such as response surface methodology (RSM), artificial neural networks (ANN) and genetic algorithms (GA) are capable of modelling and optimizing the composition of heterogeneous catalysts.⁴⁰ ANN recognizes, classifies and generalizes patterns. It reduces experimental noise and can approximate the performance outside the range of the factor input space.39,41 The technique does not require knowledge of the phenomenological equations the describe the process hydrodynamics or the reaction kinetics.⁴¹ ANN is widely applicable in science and technology fields such as economics, chemistry, separation, chemical engineering, reaction engineering, computer science, water and waste-water treatment.42-52

Rostamizadeh *et al.* applied ANN modeling to predict methanol conversion and propylene selectivity in the methanol to propylene reaction (MTP) in a fluidized bed reactor.⁵³ Inputs included reaction conditions—temperature, flow rate, pressure,

feed concentration—and catalyst composition—metal ion ratios. The close agreement between the results and the ANN model demonstrated the applicability of this approach to describe and predict complex catalytic processes.

Multi-layer feed-forward neural networks with a back propagation training algorithm, known as back propagation neural network (BPNN) or multi-layer perceptrons (MLPs) are well established models for engineering applications.^{41,54}

BPNN consists of input data, hidden layers including neurons, and training data sets.^{41,53} It is necessary to normalize input values to start network training which acts as linear or nonlinear mathematical function to predict outputs. The training develops a model according to input data to generate a network.^{41,53} Mean squared error (MSE) and root mean squared error (RMSE) are the error functions in the algorithm to compare the model predictions and the experimental data (Fig. 1).^{40,41,53}

$$MSE = \frac{1}{n} \sum_{i=1}^{n} (m_i - M_i)^2$$
 (1)

RMSE =
$$\sqrt{\frac{1}{n} \sum_{i=1}^{n} (m_i - M_i)^2}$$
 (2)



Fig. 1 Neural network catalyst modeling flowchart.

Coupling ANN and a genetic algorithm (GA) is an intelligent approach to optimize the catalyst design of any process. In fact, the ANN model can be a fitness function for checking the GA. Hadi *et al.* coupled ANN and GA to design and optimize M-Mn/ ZSM-5 systems.⁴⁰ Niaei *et al.* designed H-ZSM-5 catalyst for the methanol to gasoline (MTG) reaction with ANN–GA.⁵⁵

Izadkhah *et al.* optimized Ag/ZSM-5 catalyst to eliminate volatile organic compounds (VOCs) by coupling the ANN–GA and included catalyst formulation, preparation conditions and loading of the metal atomic descriptors in their analysis.⁵⁶ Omata *et al.* studied the methanol synthesis and applied ANN–GA to optimize the catalyst design (Cu–Zn–Al–Sc–B–Zr) and preparation conditions including calcination temperature and precipitant concentrations.⁵⁷ However, there are no existing studies that model catalyst design and optimize the operating conditions for the gas-phase oxidation of 2MPDO to MAA. In this study, we present the experimental and modeling results for this reaction. Ultimately, GA coupled with the proposed ANN model as a fitness function optimize the input parameters and predict the output value.

2 Experimental

2.1 $Cs_x(NH_4)_{3-x}PMo_{12}O_{40}(VO)_yCu_z$ catalyst preparation

We prepared eight cesium (Cs) salted heteropoly catalysts containing vanadium(v) and copper (Cu) following a full factorial design (two-levels for each) to evaluate the catalyst performance $\label{eq:Table 2} \ensuremath{\mathsf{Table 2}}\ensuremath{\mathsf{Parameters}}\xspace$ and their levels for catalyst design and operating conditions

		Ranges and levels		
	Parameters	-1	+1	
Catalyst design	Cesium (<i>x</i>)	1	3	
	Vanadium (y)	0	1	
	Copper (z)	0	0.5	
Reaction conditions	2MPDO (%)	10	13	
	Oxygen (%)	10	13	

(Table 2).58 20 g of Na2HPMO12O40 dissolved in 25 mL of distilled water (as precursor) was added dropwise to a solution of CsNO₃-NH₄NO₃ (containing 1.87 g of CsNO₃ and 0.1 M of NH₄NO₃) until a fine precipitate formed. We then filtered and dried the thick slurry for 16 h at 120 °C and recovered $Cs_x(NH_4)_{3-x}PMo_{12}O_{40}$ solid. Then 35 mL of deionized water dissolved 2.2 g of $VOSO_4 \cdot 5H_2O$ and 1.05 g of $Cu(NO_3)_2 \cdot 3H_2O$. A solid stick pulp formed while the solution was mixed. The rotaevaporator homogenized this pulp for 3 h. It then dried and calcined at 120 °C (12 h) and 350 °C (4 h) with a temperature ramp of 2 °C \min^{-1} , respectively, to provide $Cs_{r}(NH_{4})_{3-r}PMo_{12}O_{40}(VO)_{v}Cu_{z}$

We synthesized eight catalysts following a full factorial design (2³) and measured the MAA selectivity in a fluidized bed. We refer to these catalysts as $Cs_x-V_y-Cu_z$. For example, Cs_1-V-Cu is $Cs_1(NH_4)_2PMo_{12}O_{40}(VO)Cu_{0.5}$ and $Cs_1(NH_4)_2PMo_{12}O_{40}$ is $Cs-NH_4$. Five catalysts were synthesized twice and three catalysts were synthesized three times to check the reproducibility. The MAA selectivity for the three repeats was within $\pm 5\%$.

2.2 Catalyst characterization

An Autosorb-1 measured the surface area and total pore volume by N₂ adsorption/desorption after degassing the catalysts at 200 °C. A TA-Q50IR TGA analyzed the thermal decomposition of the catalysts and their stability, and also estimated the amount of coke that built up on the catalyst surface with time. An X'pert diffractometer (XRD) characterized the crystalline structure of the materials with Cu-K α radiation ($\lambda = 1.542$ Å) at 50 kV and 40 mA. A field emission scanning electron microscope (FE-SEM) (Jeol JSM-7600TFE) imaged the surface of the fresh and used catalyst samples. An EDX detector probed the existence of coke and metal elements on the surface.

2.3 Reaction conditions and procedure

A three-zone electrical furnace maintained the reactor—a μ -fluidized bed with an inner diameter of 8 mm, 520 mm long—temperature at 250 °C (Fig. 2). All experiments lasted 100 min and the total flow rate was 210 mL min⁻¹.

A ceramic disk distributed the O_2 -Ar gas flow uniformly in the middle of the reactor to the 2 g of catalyst. Mass flow controllers metered the argon and a mixture of oxygen and argon and a thermocouple monitored the temperature. A



Fig. 2 Schematic of the experimental set-up.25

syringe pump metered the fluid to the nozzle and an argon atomized the liquid 2MPDO.

To minimize slumping the fluidized bed and optimizing the spray, we tested liquid 2MPDO/Ar_{atomization} ratios, pressure drop, and nozzle spray configurations.^{25,59} Atomizing the 2MPDO into a chamber below the nozzle distributed the fluid better than atomizing the liquid at the nozzle tip with Ar. We calculated the $U_{\rm mf}$ by monitoring the pressure drop of the bottom and top of the reactor to reach the uniform pressure.

We varied the liquid flow rate and fixed the Ar_{atomization} flow rate (20 mL min⁻¹) to identify the optimum ratio for a 0.3 mm nozzle. At liquid flow rates greater than 0.05 mL min⁻¹ the injector blocked. The optimal rate was 0.03 mL min⁻¹ at 250 °C.²⁵ The upper furnace zone maintained the reactor tube at 300 °C to minimize product condensation.

Argon purged the reactor while a furnace increased the temperature to the set point. Heat tape kept the exit line at 200 °C to prevent the product from polymerizing. Finally, the blank tests (empty bed) confirmed that the reactor was inert.

A quench condensed volatile compounds in distilled water. An HPLC measured the quantity and quality of all condensed products off-line and GC-MS measured the gas products. A mass spectrometer (MS) (Pfeiffer Vacuum Thermostar) monitored the gas phase composition on-line at a frequency of 1 Hz while a conductivity meter monitored the change in conductivity of the liquid phase on-line.

The factorial design for the feed composition considers two levels each for oxygen mole fraction (10% and 13%) and reactant mole fraction (10% and 13%). These narrow concentrations were based on earlier screening tests that identified these range of conditions as optimal (Table 2). Because the relative importance of these two factors were unknown we adopted a 2^2 Table 3 Optimal GA parameters applied in optimization procedure⁴⁰

Parameter	Value or type			
Population type	Double vector			
Crossover fraction	0.8			
Fitness scaling	Rank			
Mutation	Gaussian			
Selection	Stochastic uniform			
Crossover function	Scattered			

factorial design rather than a mixture design. We varied the Ar flow rate in order to achieve the desired feed concentrations.

2.4 Computational method

The Genetic Algorithm method proposes approximate solutions for optimization problems. This technique is a global search method and a special class of evolutionary algorithms. Based on biological sciences, evolutionary processes can be translated to design strategies and effective search. The GA applies these strategies and determines an optimal solution for any multidimensional problems. The GA as a search algorithm mimics the behavior of natural selection. Population generation of possible solutions by the GA leads to the best solution of problems which is the maximum of a function. Through mutation and crossover processes, better solutions are found from the current possible solutions. The process is repeated to find an acceptable solution. Here, in order to find the optimal catalyst design, we coupled the ANN model with the GA. The GA provided virtual catalysts, and the ANN model acted like a virtual catalyst test setup, which evaluated the fitness of the GA (in terms of selectivity to MAA). 2MPDO and oxygen concentrations as well as the three metal ions (Cs, V and Cu) comprise the six genes of each chromosome in the GA structure. The optimal GA procedure is:

(1) Generate a random initial population of chromosomes.

(2) Calculate MAA selectivity for all chromosomes by the ANN model.

- (3) Select the best pairs.
- (4) Perform the crossover.
- (5) Perform the mutation.

(6) Evaluate the termination criteria (convergence of population, termination of the number of generation, lack of changes in fitness value). If these are acceptable, then the program ends, otherwise it goes back to stage 2.

(7) The optimization was carried out by GA codes available in the optimization tool box in MATLAB®.

The optimal parameters of the GA are shown in Table 3. Other parameters were held at their default values or types.⁴⁰

3 Results and discussions

3.1 Catalyst composition and reaction conditions evaluation

We tested four feed compositions over eight catalysts at 250 $^{\circ}$ C to measure the product selectivity after 100 min. We maintained the oxygen at a mole fraction of 0.1 and 0.13 to simulate



Fig. 3 Feed compositions evaluation over prepared catalysts at 250 °C.

a recycle process (with partial oxygen conversion). HPLC detected MAA, MAC, 2-methylpropanal and unreacted hydrocarbon as the main products in the liquid phase. The MS detected CO₂, CO, CH₄ and unreacted O₂ in the gas phase. A stream of oxygen diluted in argon (21%) regenerated the used catalyst at 320 °C to remove coke and the MS recorded the CO₂, CO and O₂ signals to qualify the carbon and hydrogen and close the mass balance.

The maximum selectivity to MAA and MAC was 41% and 33%, respectively over Cs₁–V–Cu at 2MPDO/O₂/Ar = 13%/10%/77% (Fig. 3). Lower oxygen concentrations reduced the oxidation rate of acid products to CO_x, but overall conversion was lower.



Fig. 4 Effect of catalyst composition on MAA selectivity with 2MPDO/ $O_2/Ar = 13\%/10\%/77\%$ at 250 $^\circ\text{C}.$

Among the eight catalyst compositions, those containing both cesium and ammonium, and vanadium and copper (Cs₁– V–Cu) performed the best: and the least 2MPDO conversion (63%) (Fig. 4). The CPM catalyst was almost unselective to MAA, and its selectivity to MAC was 6%.

Partial cesium insertion into the Keggin-structure had a positive effect on thermal stability and catalyst activity. The complete substitution of Cs with ammonium had a negative effect on performance, due to the complete elimination of the active phase $((NH_4)_3PMo_{12}O_{40})$. Vanadium as an oxidant and copper as a promoter increased selectivity to desired products (Fig. 4).

Vanadium and copper have a synergistic effect on conversion in catalysts with cesium and ammonium. Neither have an effect on catalysts without ammonium. Ammonium attenuates the catalyst activity: CPM catalyst (no ammonium) produces CO_2 and methane.



Fig. 5 Gas and liquid selectivities versus time (2MPDO/O_2/Ar = 13%/ 10%/77% at 250 $^\circ C$ over Cs1–V–Cu).



Fig. 6 Electro conductivity profile with 2MPDO/O2/Ar = 13%/10%/77% over Cs1–V–Cu at 250 $^\circ\text{C}.$

RSC Advances



In the first 20 min MAA selectivity was below 13% which was confirmed by the conductivity of the quench. It increased sharply to 41% thereafter (Fig. 5). Coke forms on non-selective sites in the glycerol dehydration to acrolein thereby increasing selectivity (and yield) with time.⁶⁰ Conversely, MAC selectivity is higher at the beginning and then decreases with time, which confirms that MAC is an intermediate to produce MAA. The selectivity to CO_2 decreases slightly and reaches 15% at 100 min. CO and CH_4 selectivities are invariant at 6% and 4%, respectively (Fig. 5).

These trends, confirmed by monitoring the conductivity of products online, showed low values in the first 20 min, and then a sharp increasing trend (Fig. 6). In general, the carbon balance was from 92% to 105%. Methane and 2-methylpropanal were the main by-products in gas and liquid phases, respectively.

3.2 Modeling

We manipulated the catalyst composition and reaction conditions to enhance MAA selectivity. Metal ions such as Cs, V and Cu influenced selectivity to MAA, in addition to the reaction feed composition, which were 2MPDO and oxygen concentrations. Here we optimized and simulated the catalyst components (Cs, V and Cu) to maximize the MAA selectivity by employing an ANN and GA hybrid system. The predictive ability of ANN varies with its topology, training algorithms and transfer functions. However, there is no proper method to categorize the optimal combination of these factors; therefore, we optimized

Table 4	Input and output parameters and their levels				
	Parameter	Symbol	Min	Max	
Input	Cs	х	1	3	
-	V (mole)	Y	0	1	
	Cu (mole)	Z	0	0.5	
	2MPDO (vol%)	Р	10	13	
	Oxygen (vol%)	O_2	10	13	
Output	MAA selectivity (%)	S	0.8	41	

the factors by trial and error. Table 4 illustrates the input and output parameters with min and max values.

We tested various ANN topologies and algorithms to optimize both catalyst content and feed concentration for this reaction. The number of catalyst design and operational conditions determine the number of input neurons. Rostamizadeh *et al.* claim that ANN efficiency decreases with the increase of neurons in the hidden layer (more than 20) and also the number of hidden layers.⁵³ However, Hadi *et al.* illustrated that an ANN topology with a low number of neurons in its hidden layer failed to verify the link between input and output factors.⁴⁰ We conducted several topologies and began with four neurons in the hidden layer, and then added neurons to enlarge the network until reaching the best results without over fitting. An ANN structure with one hidden layer including ten neurons was suitable (Fig. 7).

Network training applied to 70% of the data sets and testing utilized 30% of them. Among the tested structures, one hidden layer including ten neurons provided the highest accuracy for train and test data (Fig. 8).



Fig. 8 Results of different ANN structure.



Fig. 9 Comparison of different train algorithm.

Paper



Fig. 10 Correlation of the experimental and predicted data.

Proper algorithm coupling with optimal topology provides the ANN with high accuracy to predict the experimental data. We investigated the effect of various algorithms such as gradient descent with adaptive (GDA), resilient back propagation (RP), gradient descent with momentum (GDM), Levenberg–Marquart (LM) and gradient descent (GD). Among these algorithms, the LM algorithm was the most accurate for both training and test data ($R^2 = 0.97$). BPNN with one hidden layer (6-10-1) consisting of log-sigmoid (LS) and pure linear (PL) transfer functions and the LM algorithm is an optimum ANN structure to predict the selectivity of MAA (Fig. 9).

The ANN prediction results (as output) plotted *versus* the experimental data show are well correlated ($R^2 = 0.97$) (Fig. 10).

3.2.1 Sensitivity analysis. The cosine amplitude method (CAM) examined the impact of input independent variables (catalyst composition and operating conditions) on the output dependent variable (MAA selectivity). The CAM method expressed all of the data pairs to construct a data array X in common X-space: each of the elements, X_i , in the data array X is a vector of lengths of m, that is:

$$X = X_1, X_2, X_3, \dots, X_m$$
(3)

Each of the data pairs specifies a point in *m*-dimensional space in *m*-coordinates to describe the points completely.

$$X_i = X_{1i}, X_{2i}, X_{3i}, \dots, X_{mi}$$
(4)

A pairwise comparison of two data samples of *X*-space (x_i and x_j) provided each element of a relation – r_{ij} – where the strength of the relation between the data pairs is measured by the membership value expressing that strength [$r_{ij} = \mu R(x_i, y_j)$]. The CAM calculates r_{ij} from the following equation:

$$r_{ij} = \frac{\sum_{k=1}^{m} x_{ik} \times x_{jk}}{\sqrt{\sum_{k=1}^{m} x_{ik}^{2} \times \sum_{k=1}^{m} x_{jk}^{2}}}$$
(5)



Fig. 11 Significance of input parameters.



Fig. 12 The effects of 2MPDO and O₂ on MAA selectivity.

Selectivity to MAA depends on all of the independent variables (Fig. 11). In catalyst design, vanadium had a higher effect compared to other elements, followed by copper and cesium. Argon depended on the concentration of hydrocarbon and oxygen; therefore, oxygen affected the MAA selectivity more than 2MPDO.

3.2.2 Effects of pair parameters on selectivity using ANN. The optimum neural network predicts the MAA selectivity from different inputs in the domain of the training data set. The concentration of argon depends on oxygen and 2MPDO concentrations. The selectivity and yield to MAA reach maximum (41% and 63%, respectively) with the lowest partial pressure of oxygen and the highest 2MPDO concentration (Fig. 12). The oxidation rate of MAA and MAC decreases with decreasing oxygen. In this case, with higher hydrocarbon concentration (13% 2MPDO/10% oxygen), the reaction is under reducing condition and oxygen acts as a limiting reagent. Therefore, we suspect that under reducing condition we have two types of active sites on the catalyst surface that produce MAA and MAC. Less coke forms and a some of the



Fig. 13 Effects of pair parameters on MAA selectivity.

active phase oxidizes the reactant to CO_x . Conversely, under oxidizing conditions, we propose additional active sites produce CO_x . 2MPDO – as the feedstock – reacted with oxygen as well which produce also CO_x . MAA selectivity was 31%, with 10% 2MPDO and 10% oxygen. Selectivity was insensitive to 2MPDO concentration but it decreases almost proportionately with increasing oxygen, which was substantiated by the ANN modelling (Fig. 12).

ANN modeling confirmed that all metal ions had a positive effect on selectivity, particularly with both NH_4^+ and Cs in the Keggin structure (Fig. 13). However, the effect of each ion was different depending on what other ions were present. The change of colours in the contour plots represent the change of MAA selectivity: the dark blue represents the lowest selectivity and the red represents the highest selectivity. The model illustrated that selectivity was higher with catalysts where Cs partially substituted NH4⁺ compared to a complete substitution of ammonium with cesium (Fig. 13a and b). The effect of vanadium and copper was more obvious with lower cesium concentrations. For example, with complete substitution of cesium with ammonium (Cs = 3), MAA selectivity was independent of vanadium; however, with lower cesium concentrations (Cs = 1), the vanadium concentration had an effect on selectivity (Fig. 13a). The ANN showed that completely substituting ammonium with cesium decreased selectivity which agrees with the experimental measurements. This observation confirms that cesium is in the catalyst structure (Cs₃PMo₁₂O₄₀) and plays a role as a support that disperses the (NH₄)₃PMo₁₂O₄₀ active phase. Also inserting vanadium in the catalyst structure enhanced MAA selectivity but only in the presence of both cesium and ammonium (Fig. 13a). Vanadium was an oxidant in the catalyst and reduced Mo^{6+} to Mo^{5+} .

Copper had a marginal effect as a promoter over a range of Cs/NH_4^+ ratios (Fig. 13b and c). MAA selectivity is essentially constant regardless of the Cu substitution at a Cs/NH_4^+ ratio equal to 1. At higher ratios, selectivity increases slightly with higher Cu substitutions. At a $Cs/NH_4^+ = 2$, MAA selectivity doubled when the vanadium substitution increased from 0 to 0.5 (Fig. 13a) while it only increased from 12% to 13% for copper (Fig. 13b). Finally, the predicts that are correlated positively: increasing the substitution rate of each increases the selectivity (Fig. 13c).

3.3 Optimization

The ANN–GA determined that the optimal catalyst composition contains an equal moles concentration cesium, vanadium and 0.15 mole fraction of copper with respect to Cs and V: Cs(NH₄) $PMo_{12}O_{40}(VO)Cu_{0.15}$. Furthermore, the optimal feed concentration is 13%/10%/77% for $2MPDO/O_2/Ar$ (Table 5). The ANN–GA accurately predicts the experimental selectivity (42% vs. 43% for the model) which confirms the developed model is valid. It predicts that the selectivity of optimum catalyst component with 1:1:0.15 (Cs : V : Cu) would be 43% with the same conversion (63%) than the 1:1:0.5 catalyst was tested.

3.4 Catalyst characterization

3.4.1 Nitrogen adsorption/desorption analysis. The analysis of the first eight catalysts showed that the Cs⁺ increased the specific surface area of HPA catalysts compared to the parent acid; conversely, copper decreased the surface area.²⁵ The surface area ranged form 19 m² g⁻¹ to 44 m² g⁻¹.²⁵ The

Table 5 Optimum catalyst and feed conditions and selectivity to MAA

Catalyst component (mol)			Feed concentration (%)			Selectivity to MAA (%)	
Cesium (x)	Vanadium (y)	Copper (z)	2MPDO	O_2	Ar	Experimental	Predicted
1	1	0.15	13	10	77	42	43



Fig. 14 Specific surface are of fresh and used catalysts.

optimized sample (before and after reaction) represents a hysteresis loop at a relative pressure of 0.6–1, confirming type V isotherms and illustrates that this catalyst is a micromesoporous material (Fig. 14). The surface area and pore volume of the optimized catalyst is 31 m² g⁻¹ and <0.21 mL g⁻¹, respectively, and after reaction it dropped to 24 m² g⁻¹ and <0.19 mL g⁻¹.

3.4.2 XRD specification. The curves and crystalline peaks are the same for the optimized catalyst before and after reaction (Fig. 15). Each curve represents a peak in Fig. 15. The catalyst before and after reaction has a cubic lattice of ammonium oxonium molybdenum oxide phosphate ((NH₄)_{2.6}-(H₃O)_{0.4}(PO₄MO₁₂O₃₆)) with a = b = c = 11.7 Å. The thickness of each curve is the same in different positions, which suggests that the catalyst is homogeneous and all the metal ions dispersed uniformly. The main diffraction peaks are at $2\theta = 10.6^{\circ}$, 18.5° , 24.1° , 26.1° , 30.6° , 36.0° , 39.3° , 43.9° , 47.9° , 55.5°



Fig. 15 XRD diffractograms of fresh and used catalysts.



Fig. 16 FE-SEM and EDX characterization for (a) fresh and (b) used optimized catalysts and their elemental analysis. The table caption in the figures report the elemental mass fraction in %.

and 62.1°, which correlate to (110), (211), (310), (222), (400), (332), (510), (440), (532), (550) and (732), respectively.

3.4.3 Morphological analysis. The surface of the optimized catalyst before and after reaction was rough, with particle grains varying from 20 nm to 500 nm (Fig. 16). The surface did not sinter; however, higher zoom (\times 50 000) shows spherical particles cover the surface. The EDX spectrum of the catalyst (Fig. 16a and b) confirms the presence of Cs, Mo, P, V, and Cu, while the used catalyst also shows the presence of carbon.

Elemental analysis of the catalyst before and after reaction also confirms carbon deposition on the surface, with an increase in mass fraction from 3.2% to 19.5%. A small fraction of NH_4^+ remains after calcination in the catalyst (a mass fraction of 0.001) but none remains after reaction. Map analysis using an EDX detector illustrated that all ions dispersed uniformly over the catalyst surface.

4 Conclusions

A Keggin structure with cesium, vanadium and copper demonstrated the best performance for maximum selectivity to MAA (41%) with 63% conversion. MAA selectivity increased with a decrease in oxygen concentration due a drop in conversion. Methane and 2-methylpropanal (produced by thermal decomposition of the reactant and hydrogen transfer of MAC, respectively) are the main by-products. We propose a powerful ANN model to predict MAA selectivity in a fluidized bed reactor based on oxygen and 2MPDO concentration and catalyst composition. BPNN with one hidden layer (6-10-1) consisting of log-sigmoid (LS) and pure linear (PL) transfer functions and the LM algorithm is an optimum ANN structure for predicting MAA selectivity. Sensitivity analysis illustrates that the vanadium content in the catalyst structure and oxygen concentration are the most significant inputs. A genetic algorithm optimized the parameters, and the predicted selectivity to MAA was 43% over the optimal catalyst (Cs(NH₄)₂PMo₁₂O₄₀(VO)Cu_{0.5}) with 2MPDO/O₂/Ar = 13%/10%/77%. At the end, we tested the optimum catalyst and the selectivity to MAA was 42% which confirmed the model predictions.

Acknowledgements

The authors would like to thank MITACS and NSERC for their financial support of this study. Also, the great efforts of Dr Cristian Neagoe and Davide Carnevali at Polytechnique Montreal for set-up, preparation, and analytic development are greatly appreciated.

References

- 1 K. Nagai, Appl. Catal., A, 2001, 221, 367-377.
- 2 J. G. John, Production of methyl methacrylate, US3075001 A, 1963.
- 3 H. H. Kung, Adv. Catal., 1994, 40, 1-38.
- 4 A. W. Smith, I. T. Jackson and J. Yousefi, *Eur. J. Plast. Surg.*, 1999, 22, 17–21.
- 5 W. Dormer, R. Gomes and M. Meek, *Methyl methacrylate: Concise International Chemical Assessment Document* 4, 1998.
- 6 N. Mizuno and H. Yahiro, J. Phys. Chem. B, 1998, 102, 437-443.
- 7 Q. Deng, S. Jiang, T. Cai, Z. Peng and Z. Fang, *J. Mol. Catal. A: Chem.*, 2005, **229**, 165–170.
- 8 F. Cavani, Catal. Today, 2010, 157, 8-15.
- 9 N. Mizuno, M. Tateishi and M. Iwamoto, *J. Catal.*, 1996, **163**, 87–94.
- 10 C. Knapp, T. Ui, K. Nagai and N. Mizuno, *Catal. Today*, 2001, 71, 111–119.
- 11 L. Wood, Methyl methacrylate market report.
- 12 F. Merger and H.-J. Foerster, Process for the preparation of alpha-alkyl acroleines, EP 0058927 B1, 1984.
- 13 R. A. Montag and S. T. Mckenna, Catalyst for production of alpha,beta-ethylenically unsaturated monocarboxylic acid, EP0255395 B1, 1991.
- 14 E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663–682.
- 15 G. McGarvey and J. Moffat, J. Catal., 1991, 132, 100-116.
- 16 M. Sultan, S. Paul, M. Fournier and D. Vanhove, *Appl. Catal.*, *A*, 2004, **259**, 141–152.
- 17 F. Cavani, R. Mezzogori, A. Pigamo, F. Trifirò and E. Etienne, *Catal. Today*, 2001, **71**, 97–110.
- 18 M. Misono, Chem. Commun., 2001, 1, 1141-1152.
- 19 M. Kanno, T. Yasukawa, W. Ninomiya, K. Ooyachi and Y. Kamiya, *J. Catal.*, 2010, **273**, 1–8.

- 20 H. Zhang, R. Yan, L. Yang, Y. Diao, L. Wang and S. Zhang, *Ind. Eng. Chem. Res.*, 2013, **52**, 4484–4490.
- 21 S. Paul, W. Chu, M. Sultan and E. Bordes-Richard, *Ind. Eng. Chem. Res.*, 2010, **53**, 2039–2046.
- 22 N. Mizuno and M. Mison, Chem. Rev., 1998, 98, 199-218.
- 23 N. Mizuno, W. Han and T. Kudo, J. Catal., 1998, 178, 391–394.
- 24 J.-L. Dubois, Method for producing methacrolein and/or methacrylic acid, 2014.
- 25 M. J. D. Mahboub, G. S. Patience and J.-L. Dubois, *Catal. Sci. Technol.*, 2016, **6**, 6525–6535.
- 26 N. Ballarini, F. Candiracci, F. Cavani, H. Degrand, J.-L. Dubois, G. Lucarelli, M. Margotti, A. Patinet, A. Pigamo and F. Trifiro, *Appl. Catal.*, A, 2007, 325, 263–269.
- 27 I. Kozhevnikov, K. Kloetstra, A. Sinnema, H. Zandbergen and H. van Bekkum, *J. Mol. Catal. A: Chem.*, 1996, **114**, 287–298.
- 28 T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru and M. Misono, *Chem. Mater.*, 2000, **12**, 2230–2238.
- 29 T. Okuhara, Chem. Rev., 2002, 102, 3641-3665.
- 30 J. E. Lyons, A. F. Volpe, P. E. Ellis and S. Karmakar, Conversion of alkanes to unsaturated carboxylic acids over heteropoly acids supported on polyoxometallate salts, US5990348 A, 1999.
- 31 F. Jing, B. Katryniok, F. Dumeignil, E. Bordes-Richard and S. Paul, *J. Catal.*, 2014, **309**, 121–135.
- 32 F. Jing, B. Katryniok, E. Bordes-Richard and S. Paul, *Catal. Today*, 2013, **203**, 32–39.
- 33 A. Bruckner, G. Scholz, D. Heidemann, M. Schneider,
 D. Herein, U. Bentrup and M. Kant, *J. Catal.*, 2007, 245, 369–380.
- 34 Q.-T. Huynh, Y. Schuurman, P. Delichere, S. Loridant, J. Marc and M. Millet, *J. Catal.*, 2009, 261, 166–176.
- 35 J.-S. Min and N. Mizuno, Catal. Today, 2001, 66, 47-52.
- 36 E. Etienne, F. Cavani, R. Mezzogori, F. Trifiro, G. Calestani, L. Gengembre and M. Guelton, *Appl. Catal.*, A, 2003, 256, 257–290.
- 37 M. Langpape and J.-M. M. Millet, *Appl. Catal., A*, 2000, **200**, 89–101.
- 38 Q.-T. Huynh, A. Selmi, G. Corbel, P. Lacorre, J. Marc and M. Millet, *J. Catal.*, 2009, 266, 64–70.
- 39 M. Rostamizadeh and S. M. H. Rizi, *J. Membr. Sci.*, 2012, **403**, 146–151.
- 40 N. Hadi, A. Niaeia, S. R. Nabavi, R. Alizadeh, M. N. Shirazi and B. Izadkhah, *J. Taiwan Inst. Chem. Eng.*, 2016, **59**, 173– 185.
- 41 M. Rostamizadeh, M. Rezakazemi, K. Shahidi and T. Mohammadi, *Int. J. Hydrogen Energy*, 2013, **38**, 1128–1135.
- 42 A. Ahmadpour, N. Jahanshahi, S. Rashidi, N. Chenarani and M. J. D. Mahboub, *Adsorpt. Sci. Technol.*, 2014, 32, 275–290.
- 43 S. Rashidi, A. Ahmadpour, N. Jahanshahi, M. J. D. Mahboub and H. Rashidi, *Sep. Sci. Technol.*, 2015, **50**, 110–120.
- 44 A. Corma, J. Serra, P. Serna, S. Valero, E. Argente and V. Botti, *J. Catal.*, 2005, **229**, 513–524.
- 45 J. Misra and I. Saha, Neurocomputing, 2010, 74, 239-255.
- 46 Y. E. Hamzaoui, J. Hernandez, S. Silva-Martinez, A. Bassam, A. Alvarez and C. Lizama-Bahenaa, *Desalination*, 2011, 277, 325–337.

- 47 P. Shabanzadeh, R. Yusof and K. Shameli, *RSC Adv.*, 2015, 5, 87277–87285.
- 48 A. N. Sarve, M. N. Varma and S. S. Sonawane, *RSC Adv.*, 2015, 5, 69702–69713.
- 49 M. Adabi, R. Saber, M. Naghibzadeh, F. Faridbod and R. Faridi-Majidi, *RSC Adv.*, 2015, 5, 81243–81252.
- 50 A. Asfaram, M. Ghaedi, M. H. A. Azqhandi, A. Goudarzic and M. Dastkhoona, *RSC Adv.*, 2016, **6**, 40502–40516.
- 51 A. Ahmadpour, A. Okhovat and M. J. D. Mahboub, *J. Phys. Chem. Solids*, 2013, **74**, 886–891.
- 52 A. Ghasemi, A. Saeedi and M. Moghiman, *Journal of the Chinese Society of Mechanical Engineers*, 2011, **32**, 303–312.
- 53 M. Rostamizadeh, D. C. Boffito, G. S. Patience and A. Taeb, J. Chem. Proc. Eng., 2014, 1, 201.
- 54 H. Orkcu and H. Bal, Expert Syst. Appl., 2011, 38, 3703-3709.

- 55 S. M. Mousavi, A. Niaei, D. Salari, P. N. Panahi and M. Samandari, *Environmental Technology*, 2013, 34, 1377– 1384.
- 56 B. Izadkhah, S. Nabavi, A. Niaei, D. Salari, T. M. Badiki and N. ÃĞaylak, *J. Ind. Eng. Chem.*, 2012, **18**, 2083–2091.
- 57 K. Omata, Y. Watanabe, M. Hashimoto, T. Umegaki and M. Yamada, *Ind. Eng. Chem. Res.*, 2004, **43**, 3282–3288.
- 58 F. Daubrege, Systeme catalytique contenant de loxygene, du molybdene et du phosphore, et son application a loxydeshydrogenation dacides carboxyliques satures ou de leurs esters, ainsi qua loxydation dalcanes, FR2756500 A1, 1998.
- 59 X. Liu, G. Xu and S. Gao, Chem. Eng. J., 2008, 137, 302-307.
- 60 M. Dalil, D. Carnevali, J.-L. Dubois and G. S. Patience, *Chem. Eng. J.*, 2015, **270**, 557–563.